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IMPROVING WATER FLOOD RECOVERY OF VISCOUS
CRUDE OILS BY CHEMICAL CONTROL

by

Gordon R. Scott

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled IMPROVING WATER FLOOD RECOVERY OF VISCOUS CRUDE OILS BY CHEMICAL CONTROL submitted by Gordon Robert Scott in partial fulfilment of the requirements for the degree of Master of Science in Petroleum Engineering.

ABSTRACT

A laboratory study was made of a number of aqueous solutions of acids and alkalis to determine their suitability for water flooding crude oil reservoirs. Tests were run using sodium hydroxide solutions to displace viscous natural crude from an artificial pack of unconsolidated core sand. Sodium hydroxide increased oil recovery on these displacement tests.

Tests indicate a change towards preferential water wetting of the sand after contact with weak sodium hydroxide solutions. The natural sand in the original state may be neutral or oil wet.

The interfacial tension between brine and asphaltic crude oil was drastically reduced after addition of alkali to the aqueous phase. The reduction of interfacial tension influences the wettability of the system and the oil recovery.

The results of the tests indicate that sodium hydroxide may develop as a practical method to increase water flood recovery. The research indicated some new problems which will have to be overcome before application of this technique to field use.

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INTRODUCTION

This study was made to determine if chemicals would influence the water flood recovery of high viscosity crude from silica sand. Sodium hydroxide solutions have been suggested by a number of authors to increase the efficiency and economics of water flooding. This work was directed toward reservoir conditions existing in the so called "heavy crude" producing area around Lloydminster.

High viscosity crude oil is found in a number of sand reservoirs in Canada. Producing heavy crude oil fields at Lloydminster, Wainwright and Chauvin are all of this nature. In addition, large oil sand deposits around McMurray and Peace River contain viscous crude. Estimated oil in place in these reservoirs exceeds 700 billion barrels(77). Sproule and Lloyd(84) note that outcrops of oil sand on Melville Island are somewhat similar in nature to the Athabasca Oil Sands, but make no estimate of reserves.

The heavy crude deposits in Alberta occur in the Lower Cretaceous epoch of the Mesozoic era. The Lloydminster and Wainwright fields produce from various sands of the Manville group, but the major producing formation is the Sparky sand bar deposit(13). The oil sands deposits at McMurray, Peace River and Wabasca(77) produce from the Wabasca-McMurray, Bluesky-Gething and Grand Rapids. The outcrops on Melville Island(84) are cross-bedded, deltaic and shoreline sands of

Triassic age.

The reservoir sands are variable from fine to coarse and from consolidated to unconsolidated. Most sections are characterized by interbedding of silt or shale in the sand lenses. The Sparky sand in the Lloydminster area is a fine to medium grained unconsolidated sandstone with shale stringers of varying thickness occurring throughout the producing section. Rock properties and fluid properties are difficult to establish for this heavy crude reservoir and as a result are not readily available.

Primary recovery of heavy crude reservoirs has been low. Secondary recovery by water flooding has not appeared attractive due to the unfavorable mobility ratio, reservoir stratification, clay blocking and possible oil wet nature of the sand. Beckstrom and Van Tuyl(8) noted that plain water floods were not as effective on asphaltic crude as on paraffinic crude. An economic, effective secondary recovery method is necessary for the heavy crude areas.

Sodium hydroxide solutions have been proposed for separating sand from oil as early as 1920 when Fyleman patented a sodium carbonate process. Since then Nutting(72), Uren and Fahmy(89) and Bartell and Miller(5)(6) have contributed new knowledge pointing out that sodium hydroxide reduces the interfacial tension between crude oil and water. In addition, sodium hydroxide increased recovery in water flood experiments

of Leach, Wagner, Wood and Harpke(59). Doscher, Labelle, Sawatsky and Zwicky(24) have field tested aqueous sodium hydroxide solutions on oil sands and report additional recoveries. Doscher and Reisberg(25) hold a patent for application of sodium hydroxide to "tar sands".

Summary

A series of tests were carried out to determine the effect of a number of acids and alkalis on the interfacial tension of local crude oils and brine. Varying concentrations of the chemicals were used in brine to find a minimum interfacial tension. Tests were done on crude oils from Swan Hills, Lloydminster and Chauvin.

An experimental core system was formed using natural sand from an Aberfeldy well, clean crude oil from the Lloydminster area and artificial brine. Plain water floods and aqueous solutions of sodium hydroxide were tested in this system.

Sodium hydroxide was found to be the most effective chemical at low concentrations for reducing the interfacial tension of brine and Chauvin or Lloydminster crude oil. A low concentration of sodium hydroxide was used in a brine flood and increased recovery was obtained from the core system.

LITERATURE REVIEW

History of Water Flooding

Water flooding was discovered by accident about 1876 in Pennsylvania. According to Palazette(75) water from an upper sand drained into the oil sand through abandoned wells where the casing was pulled. Substantial increases in production were noted on the nearby producing leases. These increases were short-lived, as the abandoning company, upon discovering that oil was being flooded off their leases, promptly reconditioned the oil wells

John F. Carll, a geologist with the Geological Survey of Pennsylvania, was the first to suggest intentional water flooding. Carll made this statement in 1880:

"The flooding of an oil district is generally viewed as a great calamity, yet it may be questioned whether a larger amount of oil cannot be drawn from the rocks in that way than by any other, for it is certain that all the oil cannot be drawn from the reservoir without the admission of something to take its place."

The first scientific approach was made in 1916 when a line drive was applied in the New York field. The five-spot pattern flood was introduced in Bradford, Pennsylvania in 1927.

Leverett(61) in 1941 presented the first elucidating mathematical developments on flow of two immiscible fluids

through porous media and the effects of capillarity and gravity. Shortly thereafter Buckley and Leverett(15) published the classic frontal displacement paper which describes the water flood process. The basic assumptions of this classic paper simplified the mathematical approach. Authors such as Douglas, Blair and Wagner(26) and others have confirmed that only small deviations from the Buckley and Leverett theory are found when the capillary pressure and gravity terms are included in the frontal displacement solution. High speed digital computers are necessary to solve the frontal displacement problem with all the influencing terms. As a result the methods of these recent authors have not come into common use.

Chemicals Used for Improving Water Flood Recovery

Chemicals have been suggested as additives for flood water as early as 1925. Patents were issued in 1920 for the use of sodium carbonate in a process described by Fyleman(35) to separate bitumen from sand. Nutting(72) in 1925 proposed similar methods for improving the recovery in water floods. Nutting suggested that water in contact with silica formed SiOOH which had an affinity for hydrocarbons and expected a surface layer of CH_3SiOOH . Tests with carbonates, bicarbonates, borates, silicates and acetates of the Group I elements showed that these chemicals destroyed the

affinity of oil for sand. Uren and Fahmy(89) further developed this hypothesis by considering the following reaction:



and



Uren supported the validity of this reaction by pointing out the loss in alkalinity when the solution was in contact with silica sand.

The early authors understood the basic concept of wettability and they believed that the interfacial tension of sand to water was reduced. By measurement they were able to determine that the interfacial tension of water and oil was reduced to a low value by NaOH. The problem of forming a bank of solution behind the flood front and the possible precipitation of calcium carbonate in the presence of calcium salts was recognized.

Beckstrom and Van Tuyl(8) confirmed these results and found that acids did not improve recovery on the systems they studied. A definite reaction between sodium carbonate and sandstone was noted, similar to that suggested by Nutting and Uren. A one-percent by weight solution of sodium carbonate resulted in the greatest water flood recovery.

The equilibrium pressure, the pressure applied to the hydrocarbon phase which prevented advance of water into a

sand filled capillary tube, of a water-hydrocarbon-sand system was increased by the addition of sodium carbonate and sodium hydroxide to the water phases. Bartell and Miller(6) found this increase to be about 25 percent when benzene was the hydrocarbon and about 33 percent for a selected crude at the hydrocarbon phase. Also it was noted that the interfacial tension of the oil-water interface decreased, but there was little effect on the benzene-water interface. Sodium hydroxide concentrations of 0.5 percent by weight reduced interfacial tension of a crude oil from 25 to 9 dynes per centimeter, while increasing equilibrium pressure by 10 percent. In view of these results(6), the chemical action producing increased recovery was associated with the aqueous solution - silica portion of the system either through adsorption or chemical reaction at the interface.

Reisberg and Doscher(80) found that sodium hydroxide solutions and hydrochloric acid solutions reduced the interfacial tension of water and Ventura crude. Above a pH of 8, no solid film formed at the oil-water interface. Glass slides wet with water, immersed in oil, reimmersed in water and allowed to drain upwards produced a more hydrophobic surface, depending on the oil exposure time. The water molecules, which were initially absorbed on the glass slide, promoted subsequent adhesion of the crude oil. Similar tests run using acidic, neutral and alkaline solutions showed there was a

considerable displacement with the alkaline solutions, but no displacement for the acidic and neutral solutions. Experimental water floods(80) of Torpedo sandstone using sodium hydroxide solution confirmed the above results and increased recovery approximately 20 percent based on pore volume. Field use was made of alkaline solutions to remove sand, water and asphalt rich sediments from tubing in the Ventura field.

A laboratory and field test of sodium hydroxide water flood solutions was carried out on the Muddy "J" sand in Nebraska. Leach, Wagner, Wood and Harpke(59) tested this reservoir and found the sand to be preferentially oil wet. Wettability reversal tests performed using the techniques outlined by Leach and Wagner(58) showed that the addition of sodium hydroxide changed the contact angle to 40 degrees from the original 135 to 170 degrees. The field test, made on a previously flooded out area, recovered a significant volume of oil after flooding with a slug of 2 percent sodium hydroxide.

Crude Oil Components Which Affect Wettability

Recognition of wettability as a major factor in secondary recovery prompted investigation into the nature of the components in the sand-water-oil system which influenced oil recovery. The first major paper was published by Benner and Bartell(9) in 1941, on the effect of crude oil components on the interfacial tensions. Components which appear most

effective as interfacial tension lowering agents are composed of a polar* portion similar in nature to water and non-polar portion similar to many organic liquids. Basic polar impurities appear to be chemisorbed at an acidic-silica interface. Silica sand is generally recognized as a hydrophilic solid.

Bartell and Nederhauser(7) found a solid film formed at crude oil-water interfaces. Water spray extraction of the crude samples yielded 0.007 percent by weight of a highly surface active film-forming material. This material was asphaltic in character and formed rigid films on water about 30 angstroms in thickness. Molecular weight of the material was 1600. Resin and asphaltene content of the crude oil was closely related to the interfacial activity.

Work done on Wilcox crude by Denekas, Carlson, Moore and Dodd(21) yielded about 0.014 percent of film forming substance. This material was mainly long chain normal paraffins of up to 80 carbon atoms. The hydrophobic film deposited on sand grains was suggested to be composed of resins and surface active materials in combination with these long chain paraffins.

Dodd, Moore and Denekas(23) further found the film forming material to contain resins, waxes, porphyrin-metal complexes and free porphyrins. The most interfacially active of these materials were the porphyrins and their metal complexes.

* unsymmetrical distribution of electrical charge on the molecule

Zinc, copper, nickel, titanium, calcium, vanadium and iron were absorbed at the water-oil interface and it was suggested these existed as porphyrin-metal chelate complexes.

A 14.1 degrees API crude yielded a considerable amount of nickel-porphyrin and vanadium-porphyrin complex which exhibited interfacial activity. Dunning, Moore and Denekas(28) found the interfacial activity and film forming tendency of the petroleum extracts to parallel their porphyrin contents. Bartell and Nederhauser(7) attempted to isolate the interfacially active materials by adsorption on activated carbon and silica gel. They found that they were unable to remove these adsorbed materials although they tried a number of solvents. Reisberg and Doscher(80) point this out as evidence that this adsorption is not a reversible process. These authors separated interfacially active material using sucrose in water and benzene. The separated fractions appeared related to resins and asphaltenes of which the interfacially active materials constituted a highly oxygenated, low molecular weight fraction.

Blakey and Lawrence(11) in 1954 found emulsification of sea water and fuel oil to be caused by an asphalt fraction containing oxygen in a saponifiable grouping. The surfactant produced by reaction of crude oil with sodium hydroxide was found to displace the interfacially active asphaltic material responsible for the rigidity of the neutral interface. A film

of water left on glass capillaries from the displacement of water by crude was 0.2 angstroms thick. When the aqueous phase used contained 1 percent sodium hydroxide the water layer was 10,000 angstroms. Similarly benzene displacing the sodium hydroxide solution left a film of 1200 angstroms.

Denekas, Mattax and Davis(22) tested various fractional distillation cuts of a number of crude oils to determine their effect on wettability. The final fractions and residues were in all cases more oil wetting than the initial fractions, however, many of the low boiling fractions also reduce the water-wettability of rock samples, indicating surface active materials can exist in a wide range of molecular weights.

The asphaltene content of a crude oil is closely related to the tendency of the crude oil to make the system oil wet. Johansen and Dunning(49) tested three crude oils in their natural and de-asphalted form. Sand in contact with de-asphalted crude was found strongly water wet but the wettability could be reversed by addition of very small amounts of natural crude. Propane precipitation of the asphalt also removed the waxes which may affect the wettability of the system.

WETTABILITY

Saturation States in Porous Media

The saturation states for porous media have been noted by Versluys(90) and can be divided into four distinct regions when two immiscible fluids are in contact, one of which is the wetting phase. The wetting phase is the one having an equilibrium contact angle with the sand which is less than 90 degrees.

Figure 1 shows the four saturation states. They are outlined as follows:

a. The saturation region where complete saturation of the wetting or the non-wetting phase exists.

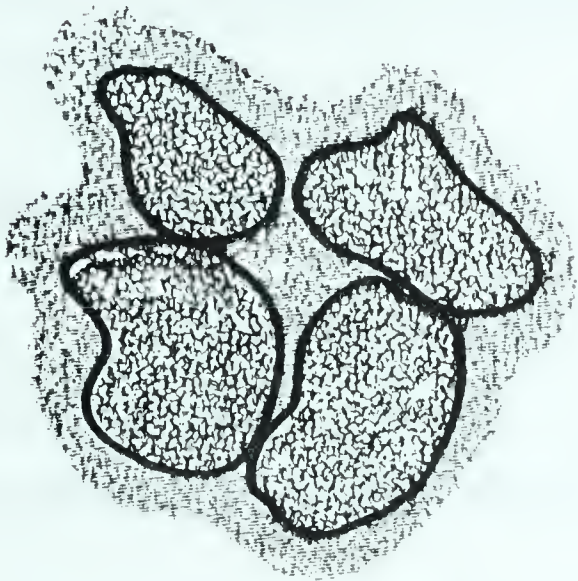
b. The pendular region where the wetting phase exists as pendular rings around the grain to grain contact points. The solid will be completely covered by wetting phase if the contact angle is zero. The wetting phase outside the pendular region is in a layer approaching molecular thickness. The wetting phase is considered immobile in this saturation region.

c. The funicular saturation regime is an intermediate region where there is a continuous network of both phases. Both phases are mobile.

d. Insular saturation is described by Pirson(76) as the region where the non-wetting phase is dispersed through

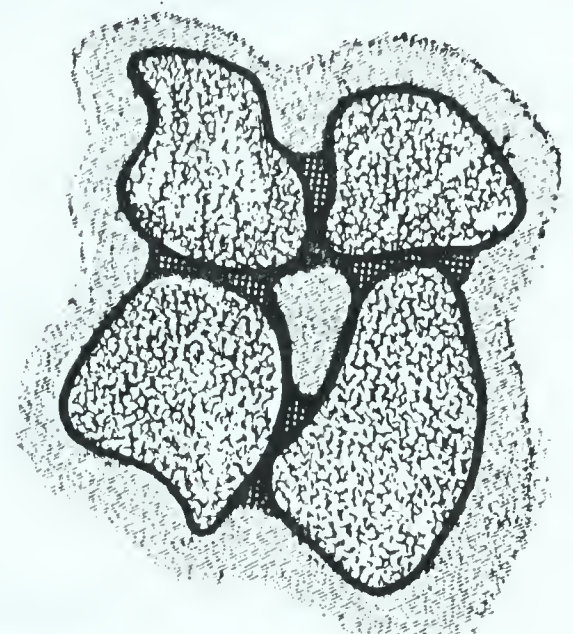
SATURATION STATES IN POROUS MEDIA

(a) TOTAL SATURATION



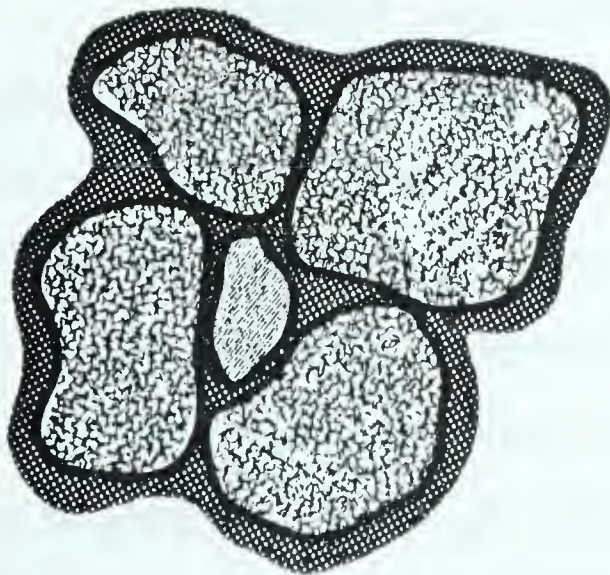
Single Phase - Continuous

(b) PENDULAR SATURATION
Wetting Phase



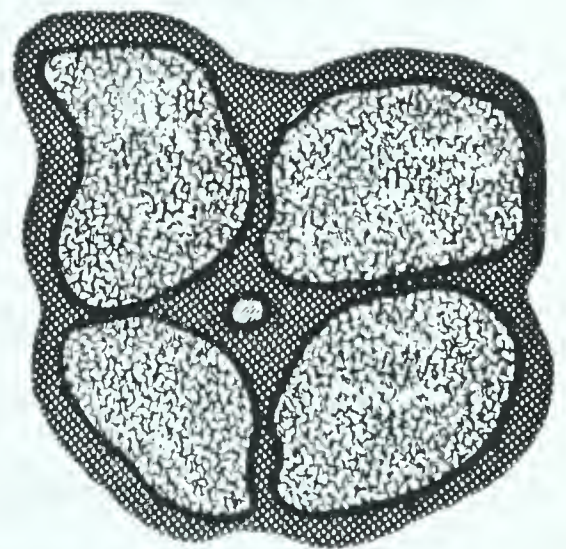
Wetting Phase - Discontinuous
Non-wetting Phase - Continuous

(c) FUNICULAR SATURATION
Both Phases



Wetting Phase - Continuous
Non-wetting Phase - Continuous

(d) INSULAR SATURATION
Non - Wetting Phase



Wetting Phase - Continuous
Non - wetting Phase - Discontinuous

 SAND PARTICLE
 WETTING PHASE
 NON - WETTING PHASE

FIG. : 1

the wetting phase in globules. The non-wetting phase is mobile when sufficient differential pressure is applied to force it through any constrictions in the interconnected pore space.

Basic Concepts

Liquid surfaces try to contract to the smallest possible area. Plateau showed that liquid surfaces always assumed a curvature where

$$\frac{1}{R_1} + \frac{1}{R_2} = \text{constant}$$

R_1 and R_2 being principal radii at any point. Geometrically it can be shown these surfaces are surfaces of minimum area for any given liquid volume.

Adam(1) explains this tendency of surfaces to contract by simple molecular theory. The molecules of a liquid are attracted by other liquid molecules in close proximity. Therefore, a surface molecule would be attracted to the side and inward. Attractive forces to the vapor phase outside the liquid are very small because of the small number of molecules and their relatively large distance apart. The resulting inward imbalance in force causes the surface to diminish in area. This contraction continues until the maximum number of molecules are on the interior.

Liquid molecules are free to move relative to one another but are attracted to each other by cohesive forces.

Solids are distinguished from liquids by the fact that solid particles are more or less fixed in their relative position to each other. Gas molecules are comparatively free from cohesive forces.

The free energy of the surface is the work done in extending the area of the surface. It is possible to replace the free energy per unit area of surface by a vector acting parallel to the surface. The units are those of surface energy (mass/time^2) or dynes per centimeter.

Surface tension is the surface energy between a substance and a vacuum. The surface energy between a liquid and a gas liquid or solid is interfacial tension. Common usage has made it customary to term the interfacial tension between a liquid or solid and air as surface tension. This term will be applied in this thesis when no ambiguity will occur.

Two immiscible liquids in contact possess free energy at the surface. This interfacial tension is always less than the highest surface tension of the two liquids because of the mutual attraction of the molecules of each liquid for the molecules of the other. The interfacial tension will depend on chemical composition and the orientation of the molecules at the interface. Antonow's rule, which states that the interfacial tension will be equal to the difference in the surface tensions, holds for many mutually saturated liquids.

The work required to separate two liquids is equal to the sum of the surface tensions of the individual liquids minus the interfacial tension of the liquid-liquid interface. Dupre's equation relates this work of separation.

Surface free energy at solid-liquid-liquid contact points can be calculated using Dupre's equation. Adam(1) develops the approach as follows:

$$\gamma_{BS} - \gamma_{AS} = \gamma_{AB} \cos \theta$$

The adhesional work is

$$W_{AS} = \gamma_A + \gamma_S - \gamma_{AS}$$

$$W_{BS} = \gamma_B + \gamma_S - \gamma_{BS}$$

$$W_{AS} - W_{BS} = \gamma_A - \gamma_B + \gamma_{AB} \cos \theta$$

For the wetting liquid to displace a non-wetting liquid it is necessary that $W_{AS} - \gamma_A$ should exceed $W_{BS} - \gamma_B$. If the liquids follow Antonow's rule

$$W_{AS} - W_{BS} = \gamma_{AB} (1 + \cos \theta)$$

where

W = work of adhesion, (ergs/cm²)

γ = interfacial tension, (dynes/cm)

θ = contact angle measured through the wetting phase

S = solid

A = preferential wetting liquid

B = non-wetting liquid

Theory of Capillarity

The pressure is greater on the concave side of a curved liquid surface than on the convex side. The pressure difference depends on the surface tension and on the curvature of the surface. Work must be done to extend the surface area as the interface moves toward the convex side. Adam(1) gives the development of the basic equation of capillarity.

$$P_1 - P_2 = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

where

P_1 = pressure on the concave side

P_2 = pressure on the convex side

R_1 and R_2 = radii of curvature

γ = interfacial tension

This can be extended to a horizontal tube of small uniform radius r where the radius of curvature is $r/\cos \theta$. Then

$$\Delta P = \gamma \left(\frac{\cos \theta}{r} + \frac{\cos \theta}{r} \right) = \frac{2\gamma \cos \theta}{r}$$

If the capillary is vertical for a static condition this driving force is balanced by the weight of the column of liquid

$$gh (D - d) = \Delta P$$

$$\frac{2\gamma \cos \theta}{r} = gh (D - d)$$

where

ΔP = displacement pressure, (gm/cm^2)

γ = interfacial tension, (dynes/cm)

θ = contact angle measured through the water phase

r = radius of capillary, (cm)

g = gravitational constant, ($\text{gm-f}/\text{gm-m})(\text{cm}/\text{sec}^2)$

h = height of liquid rise, (cm)

D, d = density of the phases, (gm/cm^3)

Capillary flow is controlled by the potential gradient and the contact angle. Benner, Dodd and Bartell(10) have shown that water will spontaneously displace oil from a capillary if the water advancing and receding contact angles are both less than 90 degrees measured through the water phase. If the water advancing contact angle is greater than 90 degrees and the receding angle less than 90 degrees, neither liquid will displace the other. When both the advancing and receding angles are greater than 90 degrees oil will displace water. This difference between the advancing and receding contact angles is quite common and is called the "hysteresis" of the contact angle.

Reviewing the various saturation regimes, the effect of contact angle and interfacial tension between the phases will be evident. When the porous media is completely saturated with either the wetting or non-wetting phase there is no liquid-liquid surface and no capillary pressure. In

the pendular saturation region the wetting phase will be immobile unless the potential gradient across the system is of sufficient magnitude to overcome capillary pressure. Both liquid phases are mobile in the funicular saturation region. Movement of the non-wetting phase in the insular saturation region is controlled by the potential gradient and the Jamin effect.

Jamin Effect

The non-wetting phase in the insular saturation region exists in the form of globules surrounded by the wetting phase. In order for these globules to move they must pass through any constrictions in the pore channel. The pressure necessary to produce movement through a horizontal constriction can be calculated using Gardescu's development:

$$\Delta P = 2\gamma \left(\frac{1}{r_1} - \frac{1}{r_2} \right)$$

where

ΔP = pressure drop across the droplet

γ = interfacial tension

r_1 = radius of curvature of the forward end
of the drop.

r_2 = radius of curvature of the larger portion
of the drop

The interfacial forces causing the Jamin effect can be a factor in the residual oil saturation remaining after water flooding a water wet system.

THEORY

Water Flooding

One of the early mathematical descriptions of fluid flow in an oil reservoir was presented by Leverett(60). This initial development turned out to be the fractional flow equation without the capillary pressure and gravity term. Leverett(61) published the complete fractional flow equation with all the terms in 1941. The fractional flow equation in its complete form is

$$f_w = \frac{1 + \frac{k_o}{q_t \mu_o} \left[\left(\frac{\partial P_c}{\partial u} \right) - g \Delta \rho \sin \alpha \right]}{1 + \frac{k_o}{k_w} \frac{\mu_w}{\mu_o}}$$

where

f_w = fraction of water in the flowing stream at any point

k_o = effective permeability to oil

k_w = effective permeability to water

q_t = total fluid flow rate per unit cross-sectional area

μ_o = oil viscosity

μ_w = water viscosity

P_c = capillary pressure

- u = longitudinal axis of the system
g = gravitational constant
 $\Delta\rho$ = density difference between the phases.
 α = angle between u and the horizontal

The signs in the numerator are dependent on the definition of capillary pressure. Leverett used

$$P_c = P_o - P_w$$

To arrive at his conclusions, Leverett assumed that the pressure differential between the two fluids is P_c , that permeability is a function of saturation alone and that Darcy's law applied.

Buckley and Leverett(15) described the mechanism of fluid displacement by taking a material balance on an elemental volume of porous media. The material balance was for water flooding.

$$\left(\frac{\partial S_w}{\partial t}\right)_u = - \frac{q_t}{\phi A} \left(\frac{\partial f_w}{\partial u}\right)_t$$

where

- t = time
 ϕ = porosity of the media
A = cross sectional area

If the capillary pressure and gravity effects are eliminated from the fractional flow equation and it is combined with the material balance, the resulting equation

relates distance, displacing fluid and saturation. Assuming fractional flow is uniquely related to saturation when capillary and gravity effects are eliminated, then

$$\Delta u = \frac{Q_t}{\phi A} \frac{df_w}{dS_w}$$

where

Δu = change in position on the flow path

Q_t = total displacing fluid entering the system

The Buckley-Leverett theory of frontal displacement is the mathematical basis used to describe immiscible displacement. Presentation of the equations in this outline follows the manner of the authors original papers.

Recently, the fractional flow equation has been put to use in its complete form, which includes the capillary pressure and gravity terms. Douglas et al(26)(27) have programmed this equation on a digital computer. Their results were found to agree closely with results obtained using the older and simpler methods of Buckley and Leverett.

EXPERIMENTAL EQUIPMENT

Displacement Tests

The core holder used for the artificial sand pack was a specially designed high-pressure stainless steel model suitable for unconsolidated sand packs. Stainless steel screen of 200 mesh was placed between the sand and the end plates which were concentrically and radially grooved to facilitate flow. The core holder was 122 centimeters long and 5 centimeters in diameter on inside dimensions.

Pressure taps were placed immediately outside the end plates on the upstream and downstream ends. Sensitive calibrated Heise gauges were connected to the pressure taps. Low viscosity white oil was used for pressure transmission.

The core assembly shown in Figure 2 was mounted in a hot air cabinet thermostatically controlled to $\pm 1.5^{\circ}\text{F}$. Heat was supplied by an intermittent, controlled electric heating element. Constant air circulation was maintained using a small fan and air ducts within the cabinet. No provision for cooling was made, so test temperatures were, of necessity, above the temperature of the surrounding room.

A constant rate Ruska proportioning pump was used to inject fluids into the core. The minimum displacement rate available using standard gears was 10 cubic centimeters per hour.

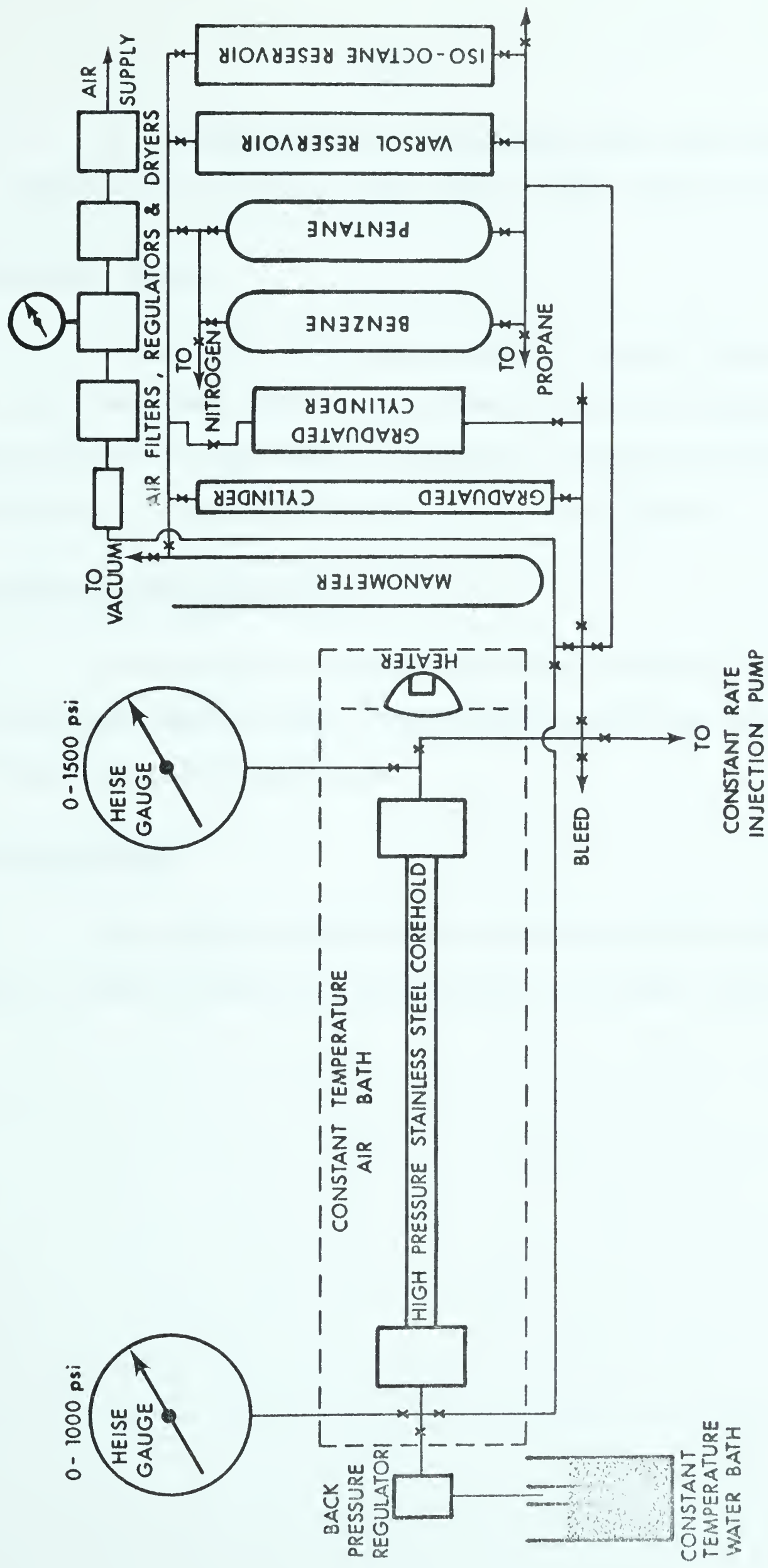


Figure 2

SCHEMATIC DIAGRAM OF DISPLACEMENT AND CLEANING EQUIPMENT
FOR AN UNCONSOLIDATED SAND CORE PACK

A thermostatically controlled water bath was used for separation of the oil and water phases after collection.

Imbibition Tests

Imbibition tests were made on a cell similar to the one described and used by Bobek, Mattax and Denekas(12). Core saturation was done on a simple vacuum cell which had provision for injection of the saturating fluid.

Interfacial Tension Tests

Interfacial tension tests were taken on a Cenco Du Nouy tensiometer model 70545 using a platinum ring, 6 centimeters in circumference.

pH Measurement

The pH was measured on a Beckman Model N pH meter using a glass reference electrode and a calomel electrode.

EXPERIMENTAL PROCEDURE

Source and Handling of Materials

Natural sand from a sparky core of the Aberfeldy A-8-30 well was used for the artificial core pack. Sand from the rubber sleeve core was cleaned in a soxlet extractor, using toluene as a solvent. After extraction the sand was passed over 25 mesh and 40 mesh Tyler sieves. It was observed that the large clay lumps were +25 mesh while the +40 mesh cut consisted of small clay lumps and a material having the appearance of asphalt residue. The -40 mesh sand and clay which formed about 90% of the total was used to pack the core.

An artificial brine was prepared for use in all tests. The brine, made up to match the chloride ion content of a field sample from the Lloydminster area described by Collins(20), contained 84.839 grams of reagent grade sodium chloride dissolved in sufficient distilled water to make up one litre. After dissolving the salt, de-aeration was necessary to remove air introduced while mixing.

Lloydminster crude oil sample No. 2426 was used for all displacement tests and some of the interfacial tension tests. This 16.0°API gravity, cleaned crude oil sample contained 0.2 percent BS and W. Chauvin crude of 22.1°API gravity, containing 2 percent BS and W, and 39.9°API gravity Swan Hills crude from Pan. Am. B.A. Cora 2-1 battery were used for

interfacial tension tests. Samples of the Lloydminster and Chauvin crude were filtered through 7 inches and 14 inches of 6-16 mesh activated alumina, respectively, for use in some of the interfacial tension tests. All samples were received and stored in closed glass or tinned containers.

Formation water used in the tests for sodium hydroxide reaction was stored in glass or pliable polyethylene containers.

Chemicals used in all tests were of reagent grade. Reagent and commercial grade solvents were used for core cleaning.

Core Packing Method

The core holder was packed with dry, cleaned, Sparky sand. For packing, the downstream end of the core holder was screwed on to the tube with the 200 mesh screen carefully placed between the tube end and the scored end cap. With the core holder in a vertical position, three heaping teaspoons of dry sand were dropped into the upper open end. The core holder was given about six sharp blows on the outside circumference at the sand surface using a large plastic mallet. To firm the sand into place it was tamped about 20 times across the sand surface using a 5/8-inch diameter metal rod. Tamping was done uniformly across the surface. The procedure of filling, tapping and tamping was repeated until the core holder was full. The upstream end of the core holder and screen were then fitted into place.

Core Handling

Gas permeability tests were run on the dry core using clean, dry air or nitrogen. Permeability was determined using the method proposed by Klinkenberg(55). Pressure taps for this core system were outside the core holder, 5 cm. from the sand faces.

The brine permeability was established by flowing brine through the core for several days at different rates and applying the "Darcy" equation. Bulk volume of the core was found by measurement. Pore volume was established by measuring the brine volume injected on the initial saturation of the dry evacuated core. This checked exactly by weighing before and after saturation. The grain volume and porosity were obtained from this data.

The core was cleaned, between brine flood No. 1 and No. 2, using about 8 pore volume of varsol, 5 pore volumes of pentane and 3 pore volumes of propane, then air dried. The core was weighed and opened. A thin layer of asphalt which had collected on the upstream face was removed. Crude oil was still evident in the core so it was recleaned. The core pack had compressed 1/2 inch making it necessary to refill the upstream end with sand. The porosity was determined on the refilled core. After saturation with brine, the core was flooded with oil to an irreducible water saturation. A material balance maintained on the core system determined the saturation at any time.

The effluent water and oil recovery was emulsified. It was found necessary in all cases to heat the stoppered graduates and effluent above 140°F to break the emulsion. Sodium hydroxide and R25 emulsion breakers were used on some graduates where chemical tests were not required. Even with the addition of these chemicals, heating was found necessary to break the emulsion.

Brine floods were made on the core before addition of any sodium hydroxide and used to establish the initial conditions and the relative permeability. Cleaning the core between brine floods No. 1 and No. 2 resulted in a small change in relative permeability but no change in initial water saturation. The data obtained from these tests were averaged to form the basic core flood for comparative purposes.

Interfacial Tension Test Procedure

Interfacial tension between various crude samples and a number of prepared brine solutions was taken using the Du Nouy ring method. In each case the ring was pulled from the aqueous phase into the petroleum phase through the interface. ASTM(3) standard method D971-50 was used for all tests. The temperature was found to be a major factor in the accuracy of the results and was closely controlled at 80°F.

For repeatability, glassware had to be carefully cleaned using petroleum solvent, soap and hot tap water, hot tap water, chromic acid, hot tap water and boiling distilled water, in order. The platinum ring was cleaned by immersing it in benzene, methyl ethyl ketone, distilled water, flaming to red heat and quenching in distilled water. This procedure made the ring water wet.

There are a number of correction factors which must be applied to the pull recorded to obtain a surface or interfacial tension value. Corrections have been made on all raw experimental data before presentation. The correction of Zuidema and Waters(94) in equation form was used. This is an extension of the work of Harkins and Jordan(43) and Freud and Freud(34) to include fluids of similar densities.

MODEL SCALING

Scaling is important in the interpretation and application of model displacement tests. Dimensional scaling allows the model to predict the performance of the actual reservoir. Engelberts and Klinkenberg(29) and other authors (38)(56)(62)(79) have discussed dimensional scaling extensively. For this study using natural sand, natural crude oil and artificial brine, the scaling of viscosity, permeability, density, capillary pressure, interfacial tension and contact angle presented no difficulty. An attempt was made to keep the properties of the system equivalent to the properties of the natural reservoir. Physical dimensions of length and thickness were fixed by the core system. Length to diameter ratio was 24.4. The primary problem was to select a displacement rate.

Displacement rate was selected by considering equipment limitations, capillary effects and viscous fingering. Rapoport and Goss(77) proposed that capillary effects influenced flood recovery according to the scaling coefficient $LV\mu_w$. In their experimental work they found that values of this scaling coefficient between 0.4 and 0.8 $\text{cm}^2\text{cp}/\text{min}$ were critical for low permeability sandstone, although values as high as 5 $\text{cm}^2\text{cp}/\text{min}$ were critical for alundum cores. Values greater than this were found to be adequately scaled. Although in our work the coefficient was 1.04 $\text{cm}^2\text{cp}/\text{min}$, it was decided that this value

was near the limit where capillary forces may not have a substantial influence on recovery.

Chouke, van Meurs and van der Poel(19) developed a scaling factor which indicates the flood conditions under which viscous forces influence flood performance. Viscous fingering will develop when the mean distance between fingers is less than the cross-sectional dimension of the core. The equation is

$$\lambda_m = C \sqrt{\frac{\gamma k}{V (\mu_o - \mu_w)}}$$

Chouke found a C value of 30 to be critical for systems which had no connate water. de Haan(40) determined C at 300 for systems with connate water. Collins(20), using a viscous crude, suggested C was 250.

For the core used in this work and the rate selected, the mean finger distance is about 1.28 cm. Viscous fingering may occur in the core and may influence breakthrough recovery but the recovery at high WOR should not be significantly affected.

de Haan also considered the scaling factor

$$I = \frac{V \mu_w L}{\gamma \sqrt{k}}$$

For values less than 10^{-1} in either intermediate or oil wet systems there was no scaling problem. The brine displacement tests of this work were taken at $I = 1.5 \times 10^{-1}$, which is near the critical found by de Haan. This would also indicate that viscous fingering could occur in the core system.

DISCUSSION

Properties of the Core System

The natural sand was sampled and a sieve analysis is presented in Table A-1. A plot of the mesh size distribution in Figure 3 shows the major portion of the sand and clay particles to be in the fine sand particle range, which is 80 to 140 U.S. Mesh. Eleven percent of the total particles were -200 mesh and classify as very fine sand, silt or clay. After the removal of the +40 portion of the core sample which was predominantly clay lumps, the sand had a fine powdery texture and the appearance of flour. After contact with water, the sand characteristic of the sample was predominant and the clay particles appeared to be concentrated in the small apertures or at the contact points where they were less visible to the eye.

Oil from the Lloydminster area is a black viscous asphaltic crude oil with a density of 0.96 grams per millilitre. The field production has a low GOR and the crude has about 10% of natural gasoline fraction (44). A crude-water emulsion forms very easily in the field production and laboratory tests. The crude sample used was cleaned to 0.2 percent BS & W at Lloydminster. The effluent from the laboratory tests was again found to be emulsified and various techniques were used to break the emulsion including heat and emulsion breakers. The crude oil may contain some surface

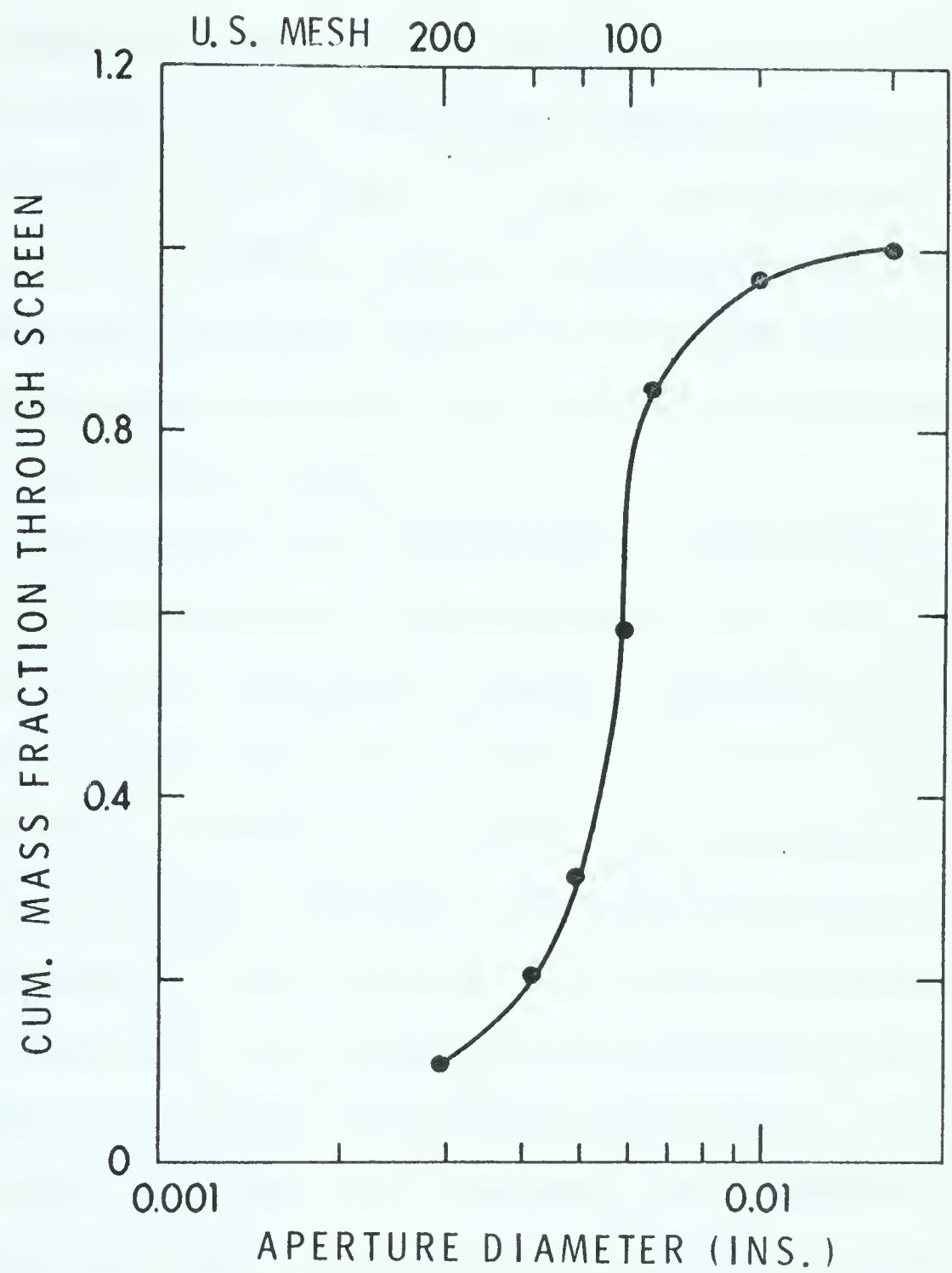


Figure 3

PARTICLE SIZE DISTRIBUTION OF ABERFELDY SAND
USED FOR CORE PACKING

active components which contribute to the formation of stable emulsions.

A sample of brine from Lloydminster was analyzed and is presented in Table D-2. The natural sample contains predominantly chloride, bicarbonate, calcium, magnesium and sodium ions. There is a noticeable absence of hydroxide and carbonate ions. For these displacement tests an artificial brine was formulated using sodium chloride with the chloride content equivalent to the natural brine.

Air permeability was established by the Klinkenberg(55) method at 187 millidarcies as shown by Figure A-1. The initial brine permeability was the same as the air permeability but decreased over several days to a stable value of 148 millidarcies. This may be evidence of either clay swelling or particle shifting in the core pack. Although some shifting was found upon opening the core pack after the first water flood it was felt that the decrease in permeability noted above was likely due to the swelling of clay particles. The sand cleaning procedure employed before packing may dehydrate the clay particles which form a portion of the system. Collins(20) had a similar decrease for the permeability of Lloydminster tank sand.

Interfacial Tension of Crude Oil and Brine

A series of tests were made to establish the influence of acid and alkali ions on crude oil-water interfacial tension. There are three interfacial forces which influence wettability or the contact angle between oil, water and sand. Water-oil interfacial tension is the most convenient of these forces to measure.

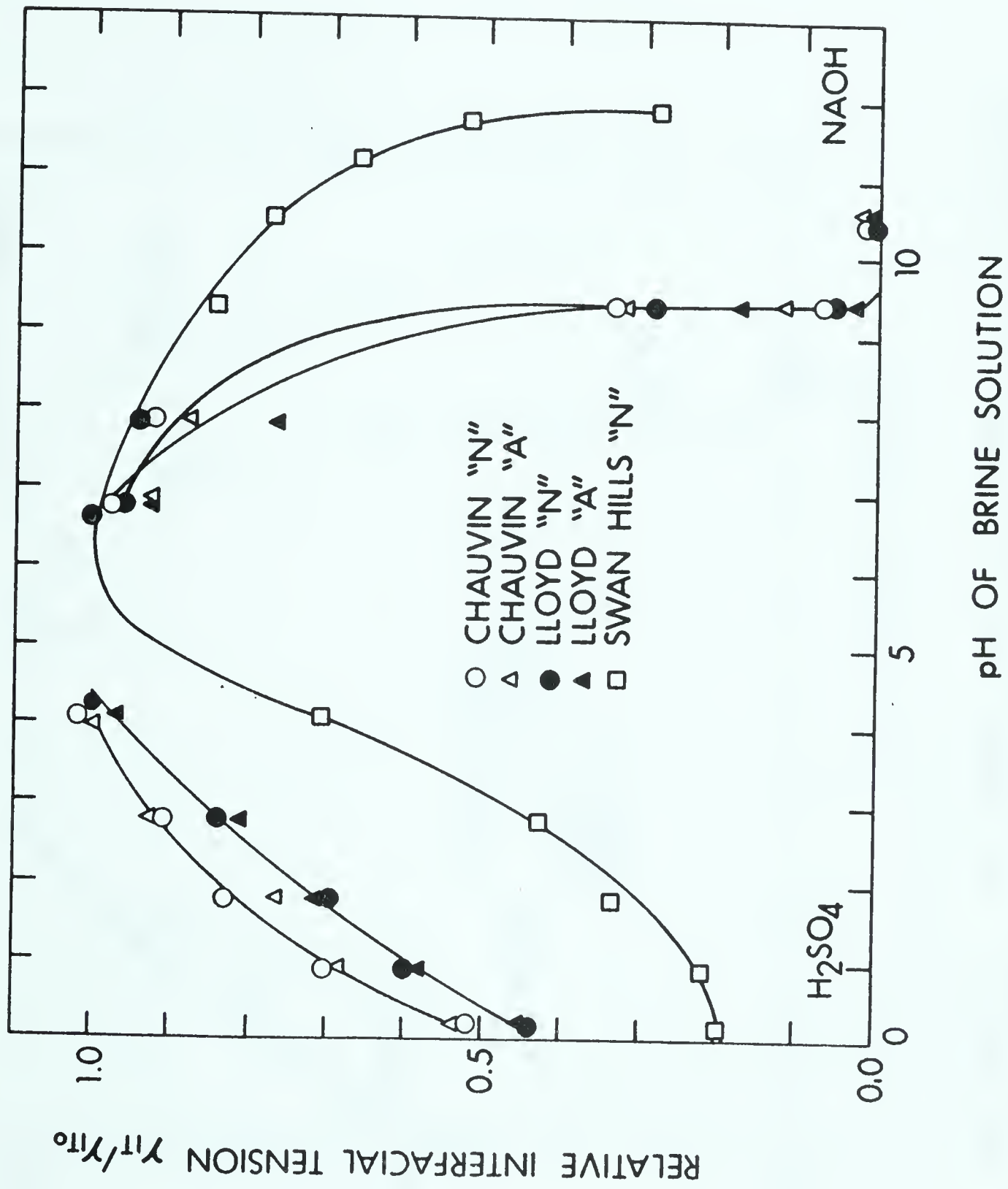
Interfacial tension between crude oil and water has a significant influence on recovery(30)(54)(70)(71). However, not all authors are in complete agreement as to the exact effect. Generally, it is agreed(30)(54)(71) that reduction of interfacial tension will increase oil recovery in an oil wet system and decrease oil recovery in a water wet system. However, Mungan(70) found an increase in oil recovery on both the oil and water wet systems with a decrease in interfacial tension. The increase in recovery was much smaller in the water wet system than in the oil wet system.

The different results outlined in the literature are possible when all the variables are considered. Variables(30) which relate closely to performance tests are interfacial tension, contact angle, velocity and viscosity. Contact angle is particularly difficult to measure and only a few authors(58)(9) have presented this type of data.

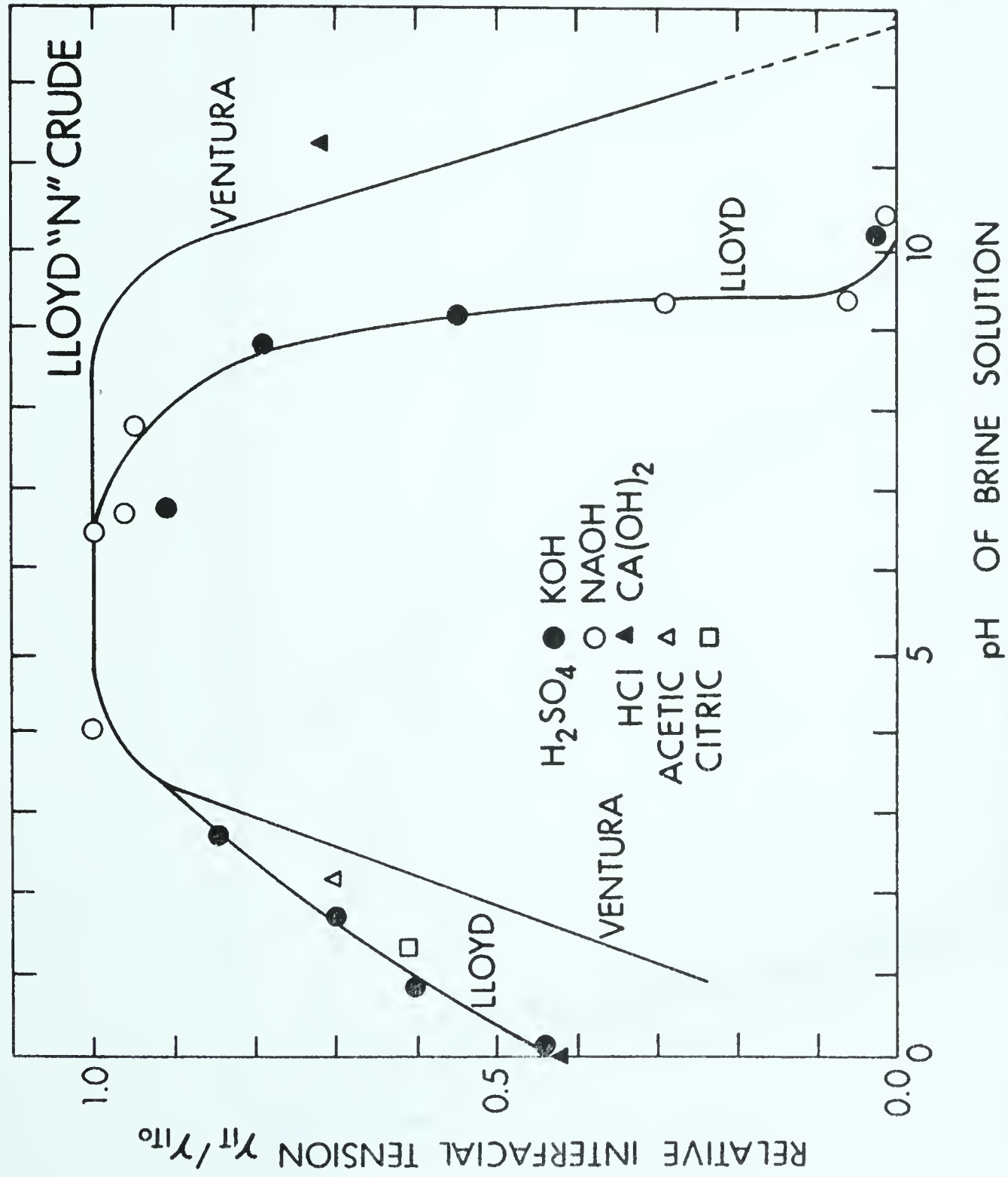
In a water wet system the residual oil exists as discontinuous globules(68)(69). This saturation state would

be insular. To remove this oil from the system either a substantial increase must be made in the pressure gradient or the interfacial tension must be reduced to a very low value(68). Most of the surface active agents reported reduce water-oil interfacial tension to about 3 dynes per centimeter. As Moore has shown this is not low enough to move the residual oil globules.

Results shown on Figures 4, 5, 6 and 7 indicate that low interfacial tensions can be achieved using sodium or potassium hydroxide on the asphaltic base Lloydminster and Chauvin crude oils. The equipment used limited the accurate gathering of extremely low interfacial tensions, however, values of less than 1 dyne per centimeter were recorded. Reisberg and Doscher(80) report interfacial tension with Ventura crude and 0.5 percent NaOH of 0.02 dynes per centimeter. This value is below the 0.03 dynes per centimeter suggested by Moore(68) as the value where residual oil can be expected to move. Lloydminster and Chauvin crudes show the same results on Figure 6 as Ventura crude with NaOH concentrations 100 times lower. Better measurement techniques may demonstrate the same low interfacial tensions for the local asphaltic crudes, possibly at much lower concentrations. Calhoun, Stahl, Preston and Neilson(17) found a similar reduction of interfacial tension using NaOH with Bradford crude.



RELATIONSHIP OF INTERFACIAL TENSION OF VARIOUS
CRUDES WITH THE pH OF BRINE



INFLUENCE OF BRINE pH ON INTERFACIAL TENSION
OF NATURAL LLOYDMINSTER CRUDE OIL COMPARED
WITH DATA OF REISBERG AND DOSCHER (80) ON VENTURA
CRUDE OIL

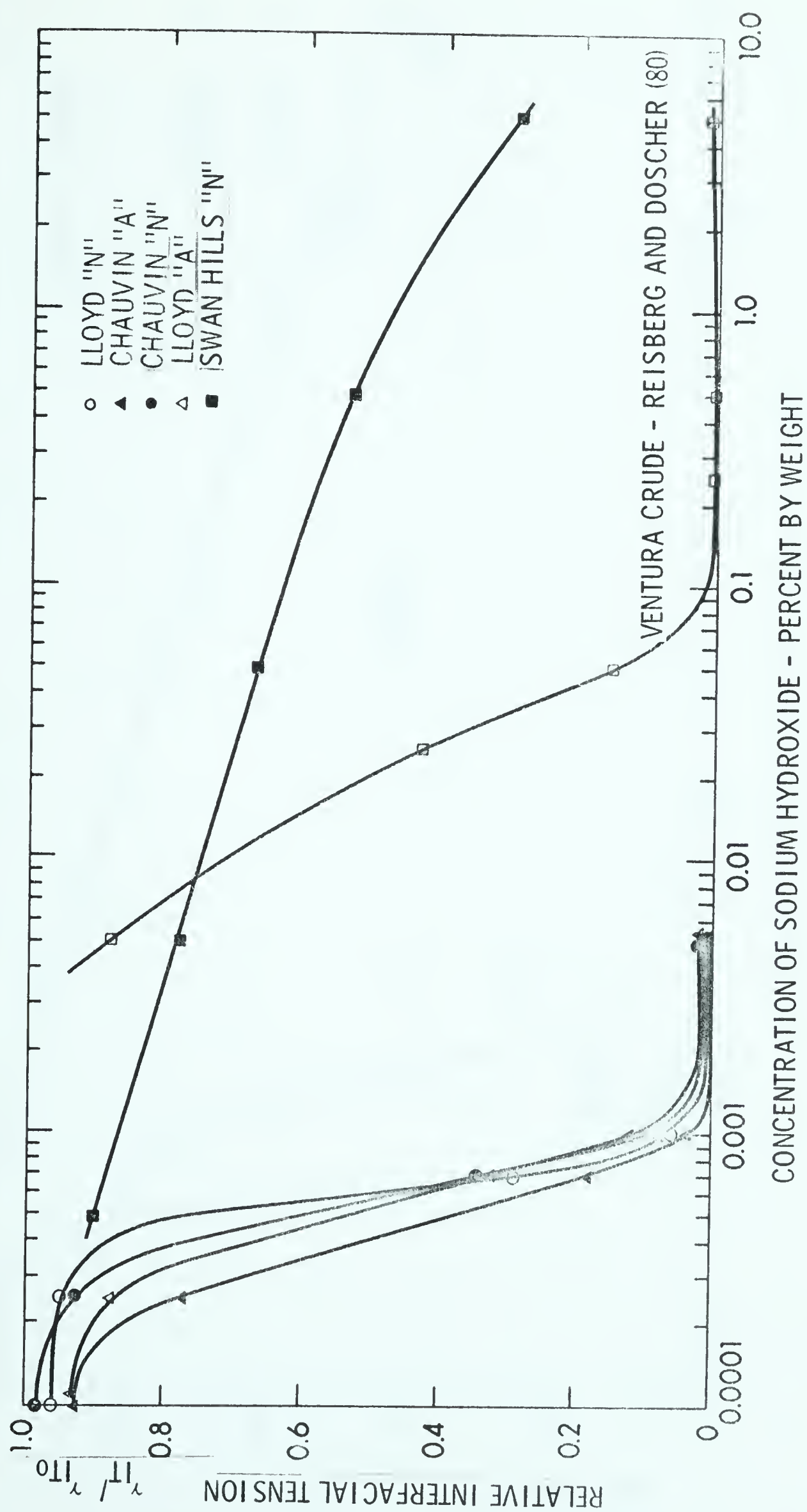


Figure 6 EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON THE BRINE-CRUDE OIL INTERFACIAL TENSION OF VENTURA AND LOCAL CRUDE OILS

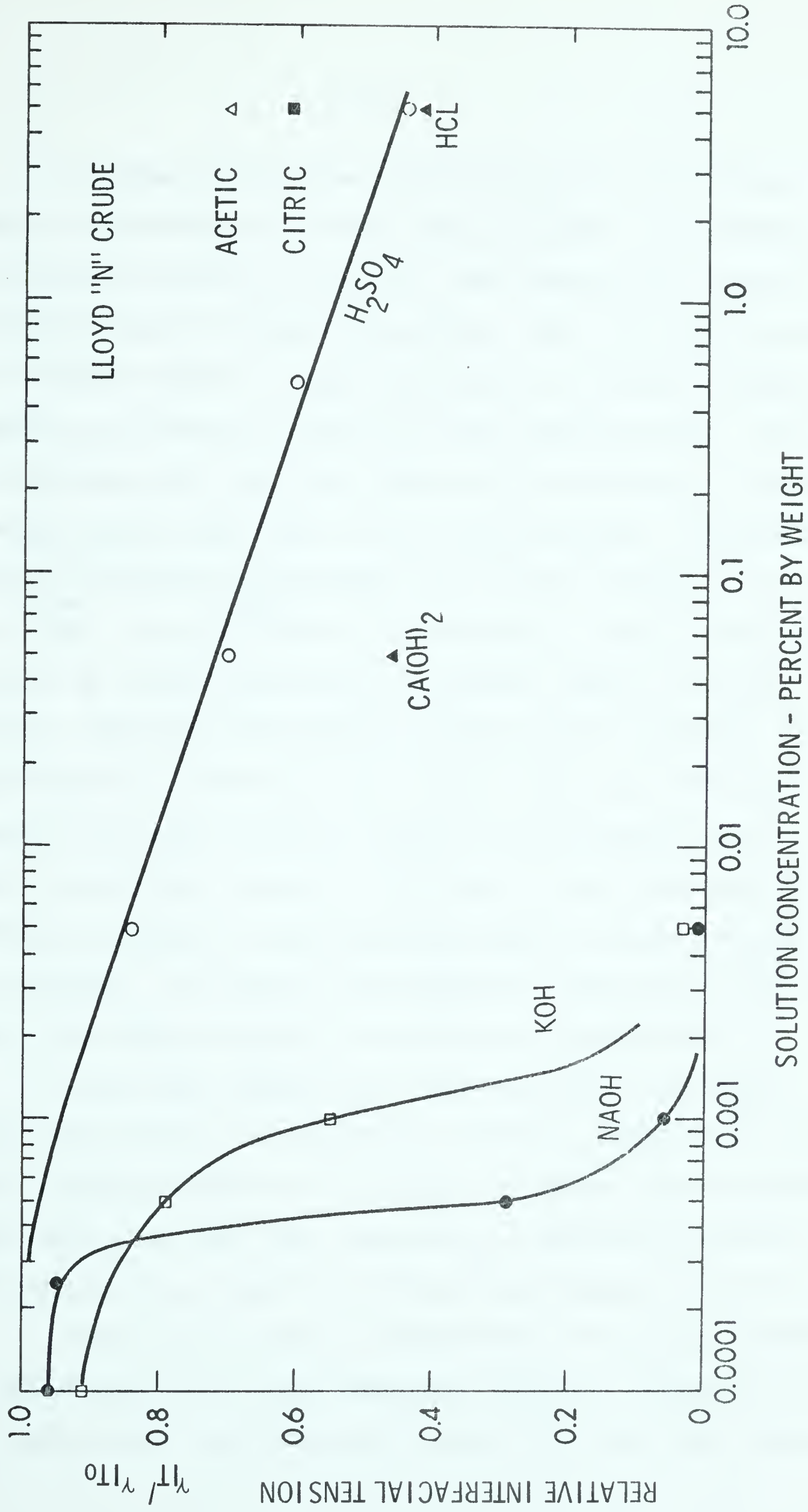


Figure 7 INFLUENCE OF ACID AND ALKALI CONCENTRATION ON THE INTERFACIAL

TENSION OF NATURAL LLOYDMINSTER CRUDE AND BRINE

Residual saturation of oil in an oil wet system has the oil distributed through the pore space in a different manner than the water wet system. The residual oil exists as a continuous phase through the system. Also, the water exists in a continuous phase through the center of the pore spaces. The system is funicular with oil as the wetting phase. To remove additional oil the water phase must penetrate or reduce the volume of the oil which is the wetting phase. Warren and Calhoun(91) relate breakthrough and ultimate recovery to $\gamma \cos \theta \sqrt{k\phi}$ and $\gamma \sqrt{\phi/k} / \cos \theta$ respectively. Any decrease in the value of these groupings of variables should increase recovery. Reducing interfacial tension should therefore increase recovery. Figures 4, 5, 6 and 7 show that addition of any of the tested acids or alkalis to the water phase reduces interfacial tension. In Figure 4 this reduction in interfacial tension is shown plotted against the pH of the brine solution. In Figure 5 Lloydminster crude oil is compared to the Ventura crude of Reisberg and Doscher(80).

Acid also reduces the crude oil-water interfacial tension. The degree of interfacial tension reduction is less for the asphaltic crude oils tested. In glass slide tests(80) it was found that acid with equivalent interfacial tension was not as effective as alkali for displacing Ventura crude oil.

Swan Hills crude oil interfacial tension was reduced more effectively with acids than with alkalis. Figures 4, 6 and 8 demonstrate the difference between the paraffinic Swan

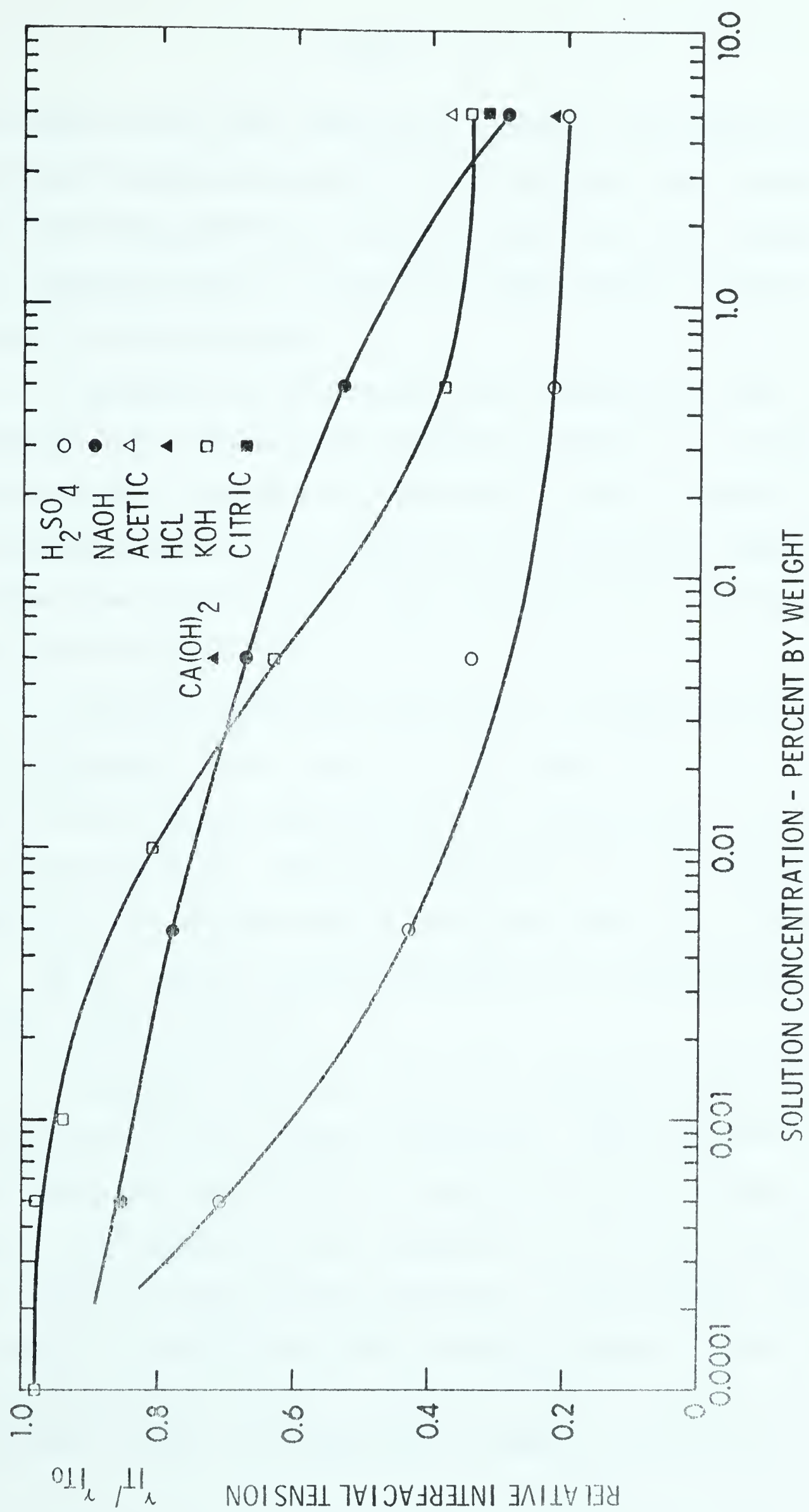


Figure 8 INFLUENCE OF ACID AND ALKALI CONCENTRATION ON THE INTERFACIAL TENSION
OF NATURAL SWAN HILLS CRUDE OIL AND BRINE

Hills crude oil and the asphaltic* crudes. One sample is insufficient to draw any general conclusions but test results indicate that the paraffinic crude oils may be less reactive with alkali solutions and as a result the interfacial tension reduction is not as great.

Figures B-1 through B-9 show additional data. The interfacial test readings are listed in Tables B-1 to B-5. Ventura crude is compared to Swan Hills crude in Figure B-1. Although one crude oil is paraffinic and the other asphaltic, they show some similarity in their reduction of interfacial tension with pH adjustment.

Calcium hydroxide was used in a number of the tests and was reported in the results, with other alkalis. It is noted that the values obtained did not always agree with the other collected data. Calcium hydroxide has a low solubility in water and the concentration chosen was near the saturation level. In all cases calcium hydroxide was less effective than the other alkalis tested.

A large number of crude oil components have been associated with film forming tendencies. Some of these components have been extracted and tested for film forming tendencies. The porphyrin metal complexes, and in particular nickel porphyrin and vanadium porphyrin complexes(28), have been found to parallel the film forming tendency of the crude.

* napthenic crude oil containing an asphalt fraction.

Hodgson, Peake and Baker(46) found a good concentration of both of these porphyrins in a typical sample of oil from the Athabasca oil sands. Vermilion crude contained 162 ppm and Lloydminster crude oil contained 240 ppm of nickel and vanadium porphyrin. These are only two of a number of possible film forming components but they indicate that the surface films associated with these crude oils could be rigid and stable.

Samples of Lloydminster and Chauvin crude oil were filtered through activated alumina in an attempt to remove some of the surface active compounds. Figure 4 shows that there was no significant change in the interfacial tension after filtering.

Imbibition Tests

Imbibition tests were run on a number of Aberfeldy sand samples using the method of Bobek, Mattax and Denekas(12). Samples were evacuated and saturated with varsol, Lloydminster crude and artificial brine. The samples saturated with hydrocarbons were contacted with brine and the brine sample was contacted with varsol. Each sample cell had about 10 cc of pore volume and 40 percent porosity after packing.

The varsol saturated sample imbibed 0.3 cc of brine after several days. Less than 0.1 cc of brine imbibed into the Lloydminster crude saturated sample. A second Lloydminster sample was tried using brine with 0.005 percent NaOH. A similar negligible amount of brine imbibed so the sample was

heated above 180°F for several days and 1 cc of the NaOH and brine imbibed. Collins(20) also found that sand saturated with Lloydminster crude was very slow to imbibe brine.

The brine saturated core imbibed varsol at a reasonable rate. One cc or 0.1 pore volume imbibed in one day.

Based on these tests the Aberfeldy A-8-30 sand appears to be neutral or slightly oil wet. Although these sand samples had been cleaned by toluene extraction, the work of Jennings(47)(48) indicates that this method of cleaning does not materially change the wettability of the system.

Brine Disaplcement Tests

Two regular water floods were run on the core pack to establish the basic characteristics of the model. The initial saturation was established by flooding the evacuated core with de-aerated artificial brine and following this with crude oil until an irreducible water was reached. (see Maguss(67)). Brine was again injected to simulate a water flood. After the first flood the core was cleaned and a second water flood performed in the same manner. The flood rate used resulted in a superficial velocity of 34 cm/day.

The connate water was 0.283 and 0.285 respectively in the regular water flood. This connate water is notably higher than that of Collins(20) due primarily to the smaller

particle size of the core and the much lower permeability. Table 1 and Figure 9 show that breakthrough occurred at 0.10 pore volume injected and the oil recovery at a water to oil ratio of 20 was 0.30 pore volume.

The work of several other investigators is shown in Figure 13. All of these results, except those of Kyte and Rapoport, were obtained using Lloydminster crude and viscosity ratios higher than 1000. The floods made using brine as a flooding agent correspond well with the production history of the initial brine floods of this work. Collins and Fazil did their tests on a 3.6 Darcy permeability core compared to 148 millidarcies for this core. The difference in absolute permeability does not appear to have a major effect on the water flood recovery. There is a notable difference between the production history of this work and that of Kyte and Rapoport. Kyte and Rapoport's work was included to show the oil recovery of a strongly water wet alundum core having a permeability of 574 millidarcies and using an oil to water viscosity ratio of 102.

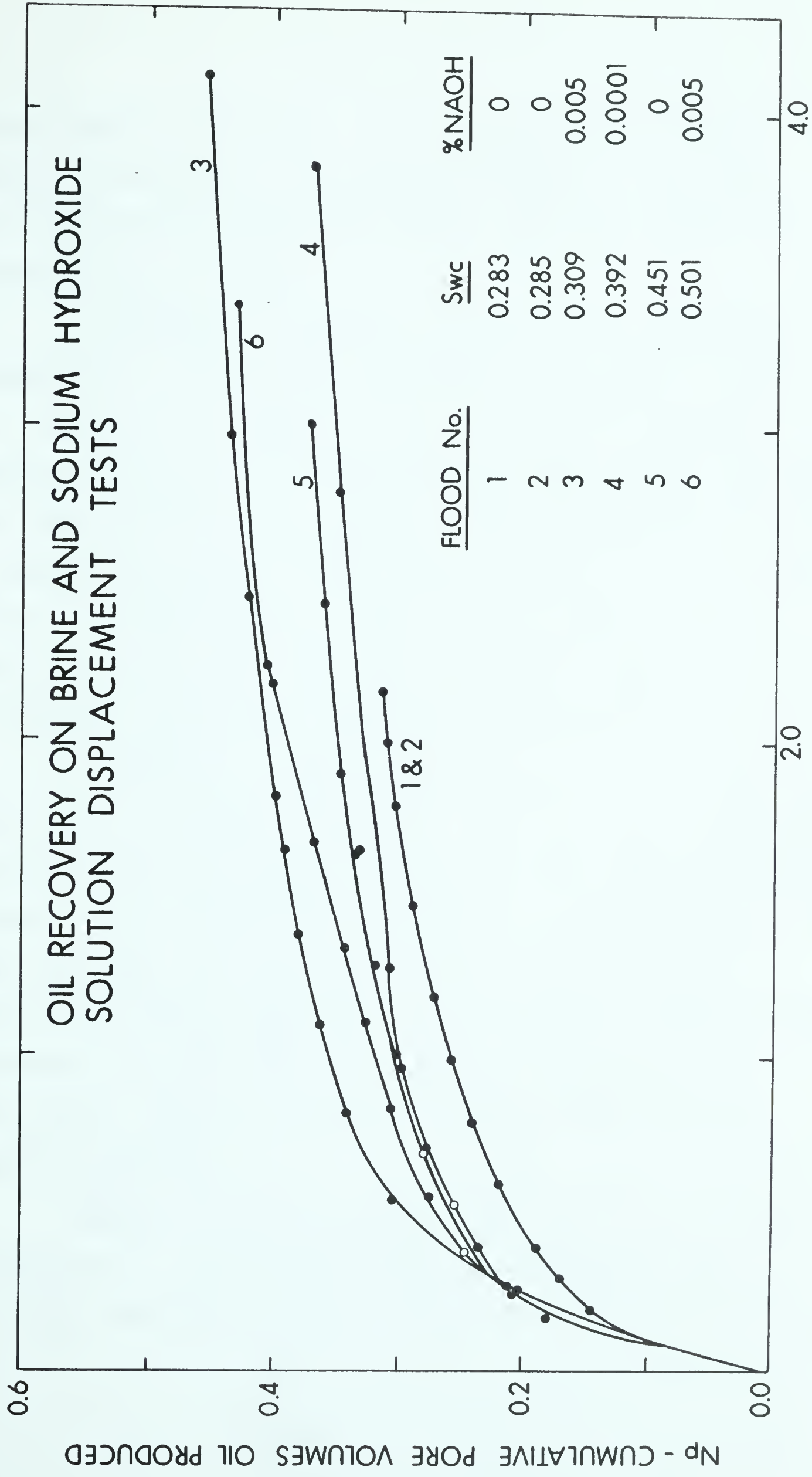
Sodium Hydroxide Displacement Tests

Results of the interfacial tension tests indicate that a very low concentration of NaOH can reduce interfacial tension. Alumina filtered Lloydminster crude with brine was reduced from 29.8 dynes/cm to less than 1 dyne/cm with 0.005%

TABLE 1

Displacement Test Performance Summary

No.	Test Type	S _{wc}	IOIP (cc)	BT PV Injected	Recovery at WOR = 20		Recovery Increase as a Percent of	
					IOIP	PV	IOIP	PV
1	Brine	0.283	638	0.10	0.397	0.285	-	-
2	Brine	0.285	630	0.11	0.430	0.310	-	-
3	0.005% NaOH	0.309	609	0.12	0.562	0.388	36%	31%
4	0.0001% NaOH	0.392	536	0.17	0.508	0.308	23%	4%
5	Brine	0.451	484	0.18	0.592	0.325	43%	9%
6	0.005% NaOH	0.501	436	0.16	0.819	0.405	98%	36%



Wi - CUMULATIVE PORE VOLUME BRINE INJECTED

FIG : 9

by weight NaOH in the brine. This very low concentration of NaOH was selected for the first flood test to determine if the interfacial tension test results would be related to displacement test recovery.

A substantial increase in recovery was noted when 0.005 percent by weight NaOH was added to the brine in Flood No. 3. Recovery at a water-oil ratio of 20 was increased 31 percent over the two previous brine floods. There was only a very small increase in recovery at breakthrough which agrees with concepts discussed in this work. Although this increase appears to be substantial in view of the extremely small amount of NaOH injected, the total recovery at WOR of 20 is only 0.39 pore volume and residual oil saturation is 0.30.

Welges(93) method was used to determine the unsteady state relative permeability. Figure 10 was constructed similar to Loomis and Crowell(66) to find the stabilized zone. A change in the slope of the fractional oil flowing curve is evident at about 0.75 pore volume brine injected. This change is not sharply defined on all floods but is sufficient to separate the stabilized portion of the flood from the frontal zone. Figure 11 shows the unstable zone relative permeability values.

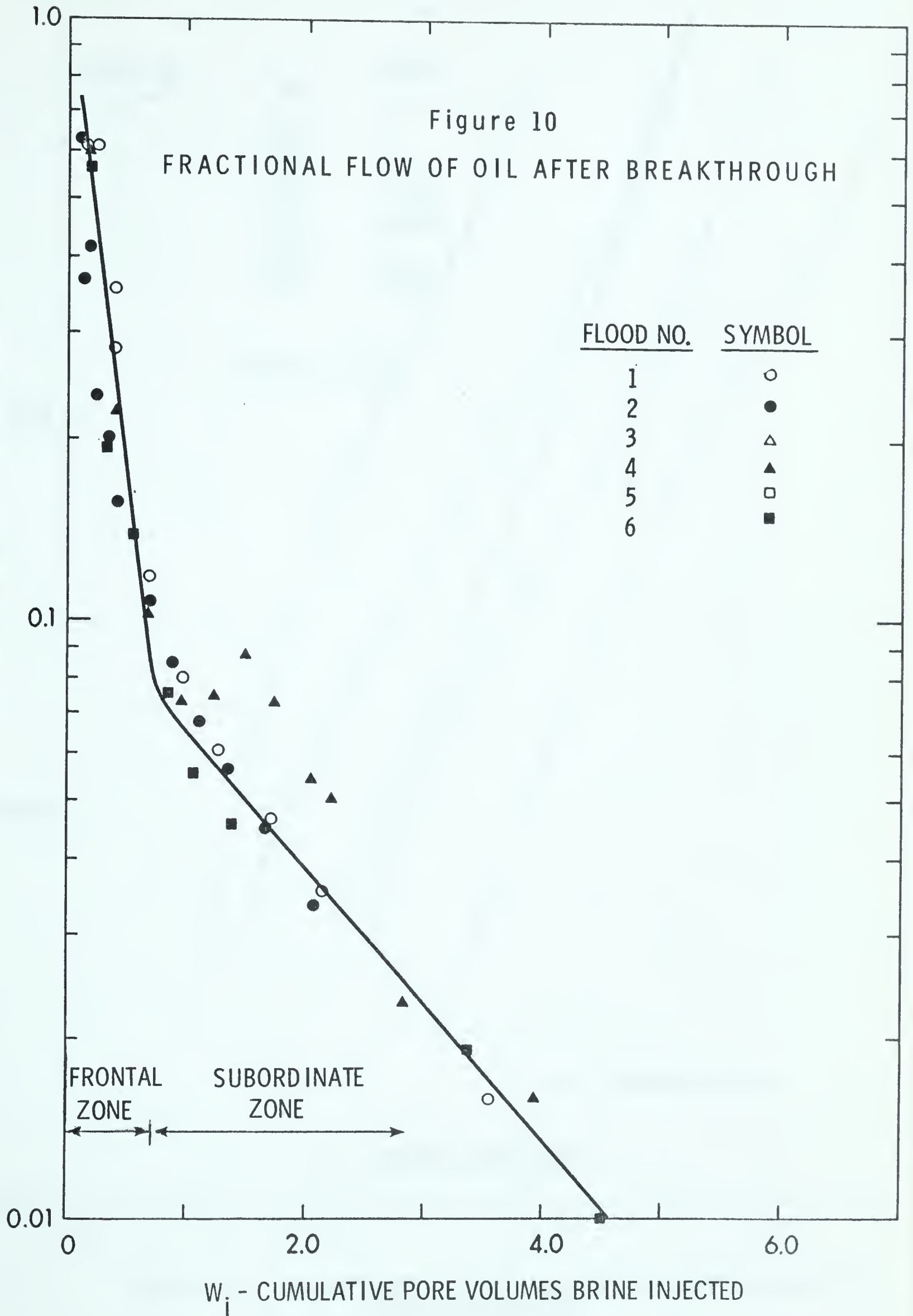
Figure 11 shows a notable shift in the k_w/k_o curve for Flood No. 3. As the NaOH diffuses through the core a bend in the curve is evident at about 0.5 water saturation.

Figure 10

FRACTIONAL FLOW OF OIL AFTER BREAKTHROUGH

f_o - FRACTION OF OIL FLOWING

FLOOD NO.	SYMBOL
1	○
2	●
3	△
4	▲
5	□
6	■



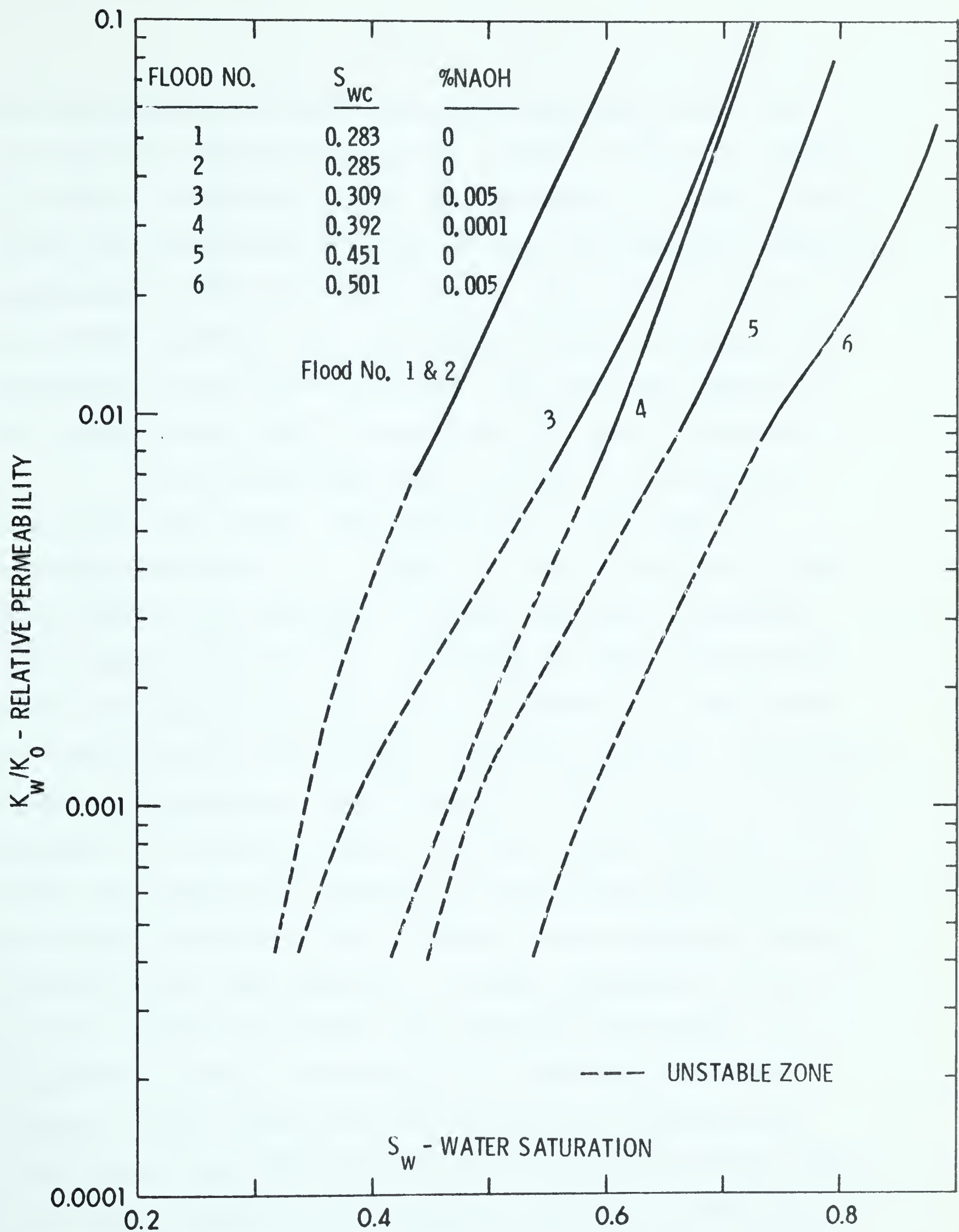


Figure 11 UNSTEADY STATE RELATIVE PERMEABILITY
WELGE METHOD

The NaOH appears to decrease the permeability to water or increase the permeability to oil. Figure 12 shows the change of relative permeability with time and amount of NaOH injected. This curve and Figures C-2 and C-3 show the change of relative permeability with increasing contact time of NaOH. All of the curves indicate that the relative permeability k_w/k_o is decreased by the addition of NaOH. This decrease appears to be related to the time of contact and the amount injected.

The permeability shift in Figure 11 is towards a more water wet system. The wettability of the core is shifting from neutral or slightly oil wet to water wet. With this shift it is reasonable to expect that the microscopic flow pattern would change. In support of these observations, Moore and Blum(68) and Chatenever and Calhoun(18) have noted and photographed these changing saturation regimes. de Haan(40) shows the microscopic fluid distribution for water and oil wet systems for viscosity ratios of one and greater than one. The water wet system has a residual oil saturation which is insular in nature regardless of the viscosity ratio although viscosity ratios greater than one tend to promote fingering. In the oil wet system the residual oil saturation is pendular or funicular in nature. According to de Haan, in an oil wet system a water filled cavity will tend to be connected by water filled constrictions to only two adjacent cavities. This will lead to separate water channels consisting of cavities connected in series.

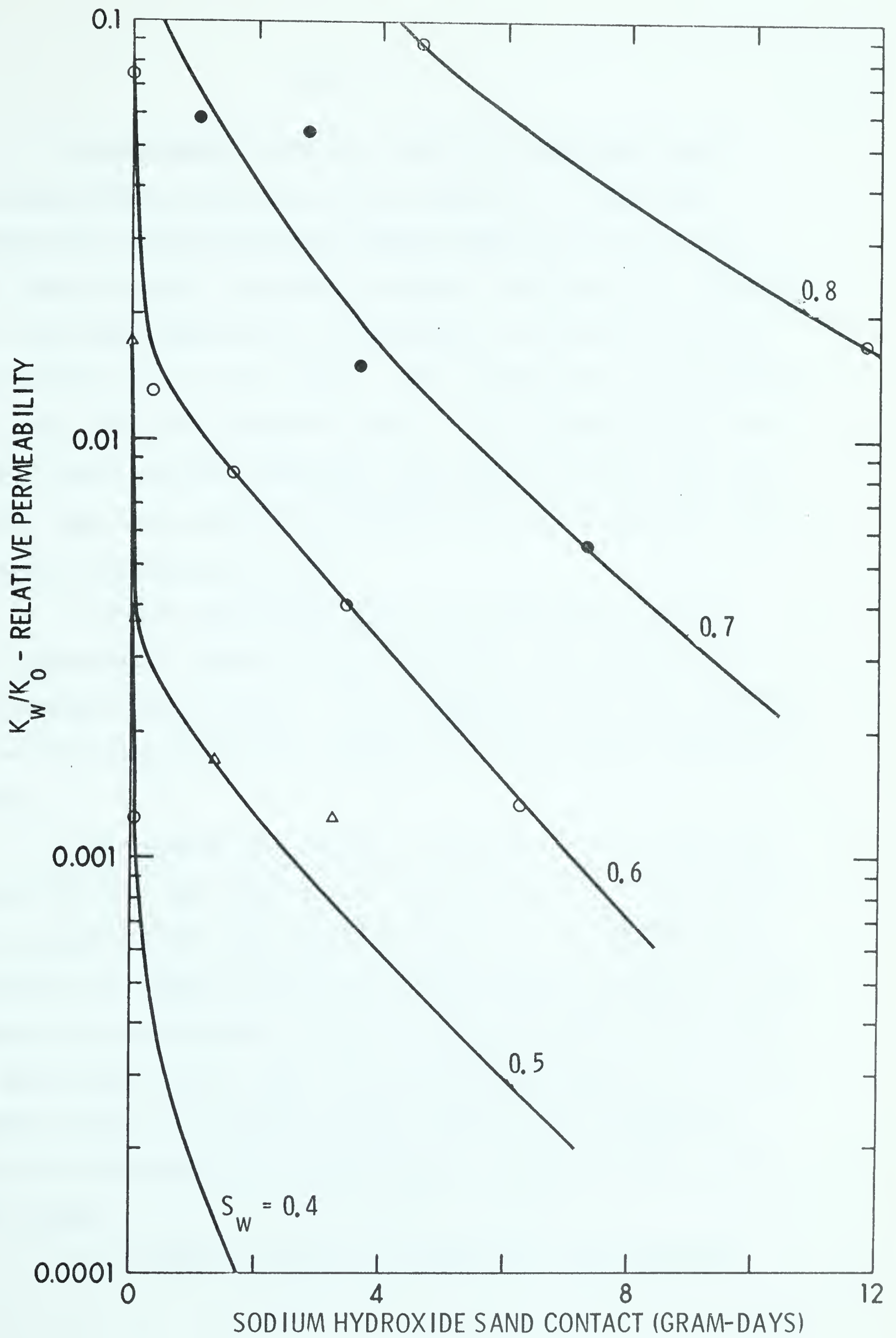


Figure 12

RELATIVE PERMEABILITY CHANGE WITH
SODIUM HYDROXIDE CONTACT

Displacement test No. 4 and all subsequent tests were made without cleaning the core system. A very weak solution of 0.0001 percent by weight NaOH was used in this test. Test results, as shown in Table 1 and Figure 9, indicate that this weak solution was insufficient to improve recovery significantly over plain water. The connate water on Test No.4 was higher than the original system. On subsequent tests the connate water further increased supporting, in part, the suggestion that the system was becoming more water wet with each subsequent displacement test.

A plain brine flood was run as Test No. 5 and a small increase in recovery was noted above the recovery of the original brine floods. It is suggested that this increase in recovery was caused by a change to water wetting characteristics.

To confirm the results of Test No. 3 a second test using 0.005 percent NaOH was run as Test No. 6. The recovery was slightly higher than found in Test No. 3. Breakthrough recoveries increased from 0.10 pore volume to 0.18 pore volume during the flood series. It is to be noted that on Test No.3, the first NaOH flood, that the breakthrough recovery was only slightly above the previous brine floods. All subsequent brine or NaOH floods had breakthrough recovers of about 0.17 pore volume.

Increased recovery using NaOH was also found by

Arana(2) using a similar system. The recovery from this test is shown in Figure 13 and is in agreement with the results of this work. Other authors(17)(59)(80)(87) have found increases in oil recovery using NaOH or a combination of NaOH and other chemicals which are usually surfactants, in the flood water.

Full consideration must be given to the fact that these test results were taken on the same core in sequence without core cleaning. Consequently any changes in the wettability or saturation state created by any one flood would influence subsequent floods. It is unlikely that cleaning the core system would have successfully restored the original sand condition. There is evidence of adsorption of NaOH which would be difficult to remove by cleaning with brine or petroleum solvents.

Water-Oil Ratio

WOR is plotted against production in Figure 14. The curves for the various floods are unique in several respects. There appears to be almost a successive decrease of WOR with successive floods. This agrees with the general results of the brine and NaOH floods and helps confirm the suggestion of increasing water wettability.

There is a distinct anomaly in Floods No. 3 and 6 and less noticeable anomaly in Flood No. 4. This maximum

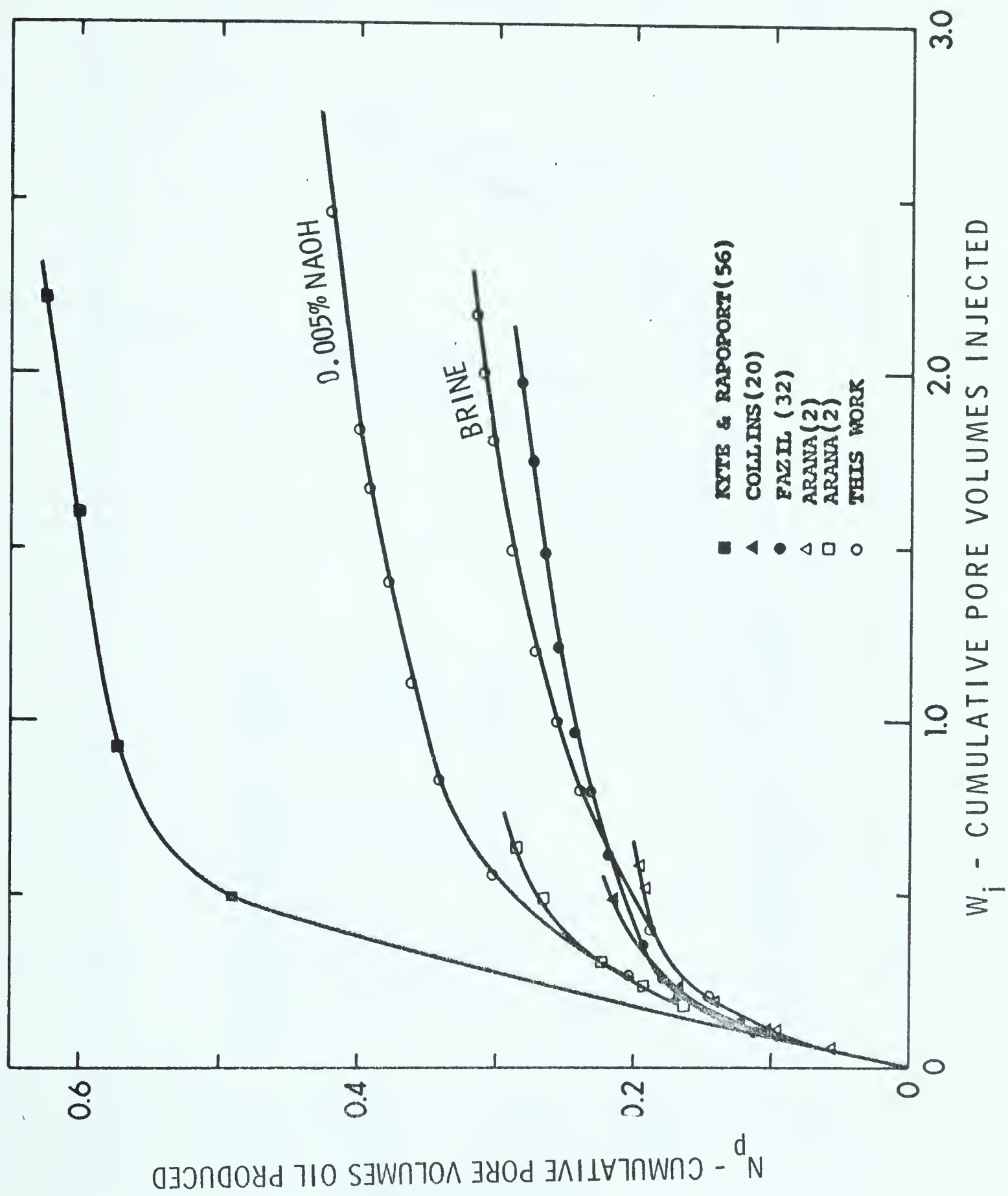


Figure 13 WATER FLOOD RECOVERY COMPARISONS

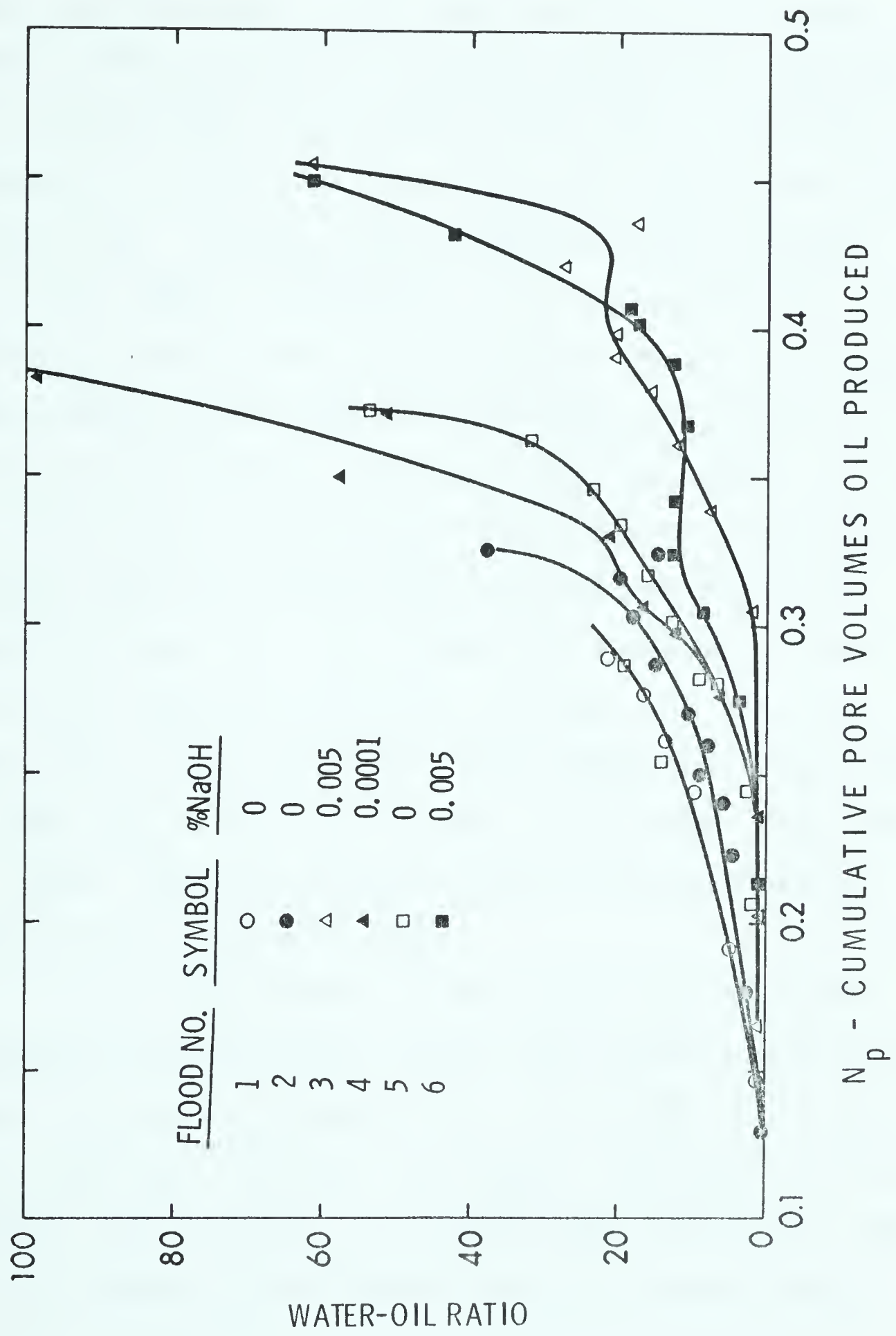


Figure 14

WATER-OIL RATIO IN RELATION TO OIL PRODUCED

point in the WOR curve could be related to the wettability reversal characteristic of the NaOH flood in this system. As the NaOH floods progressed, increasing amounts of chemicals came in contact with the surfaces of the core. The effect of the reversal is not instantaneous nor is it distributed across the flood front. A delay occurs before the full reversal effect of the NaOH is indicated. It is suggested that this time delay is due to one or more reasons. There is a chromatographic effect on the chemical injection (see Figure 15) and fingering of the brine at the flood front may prevent complete contact initially with the whole cross section of the core. In addition there is a time factor in the wettability as evidenced by Figure 23. Also there is a possibility of a connate water bank(14) behind the oil bank. At very slow flooding rates (rates below the rates employed in these tests) an oil bank may be built up in front of the NaOH. Data from Leach, Wagner, Wood and Harpke(59) may be interpreted as supporting this oil bank buildup.

On all displacement tests injectivity increased very rapidly with injection volume. The pressure drop across the core was plotted on Figure C-5. No specific trend was noted for any test, however, the rapidly increasing injectivity was general for all tests. At breakthrough injectivity was found to be several times higher than the original value.

Chromatographic Effect

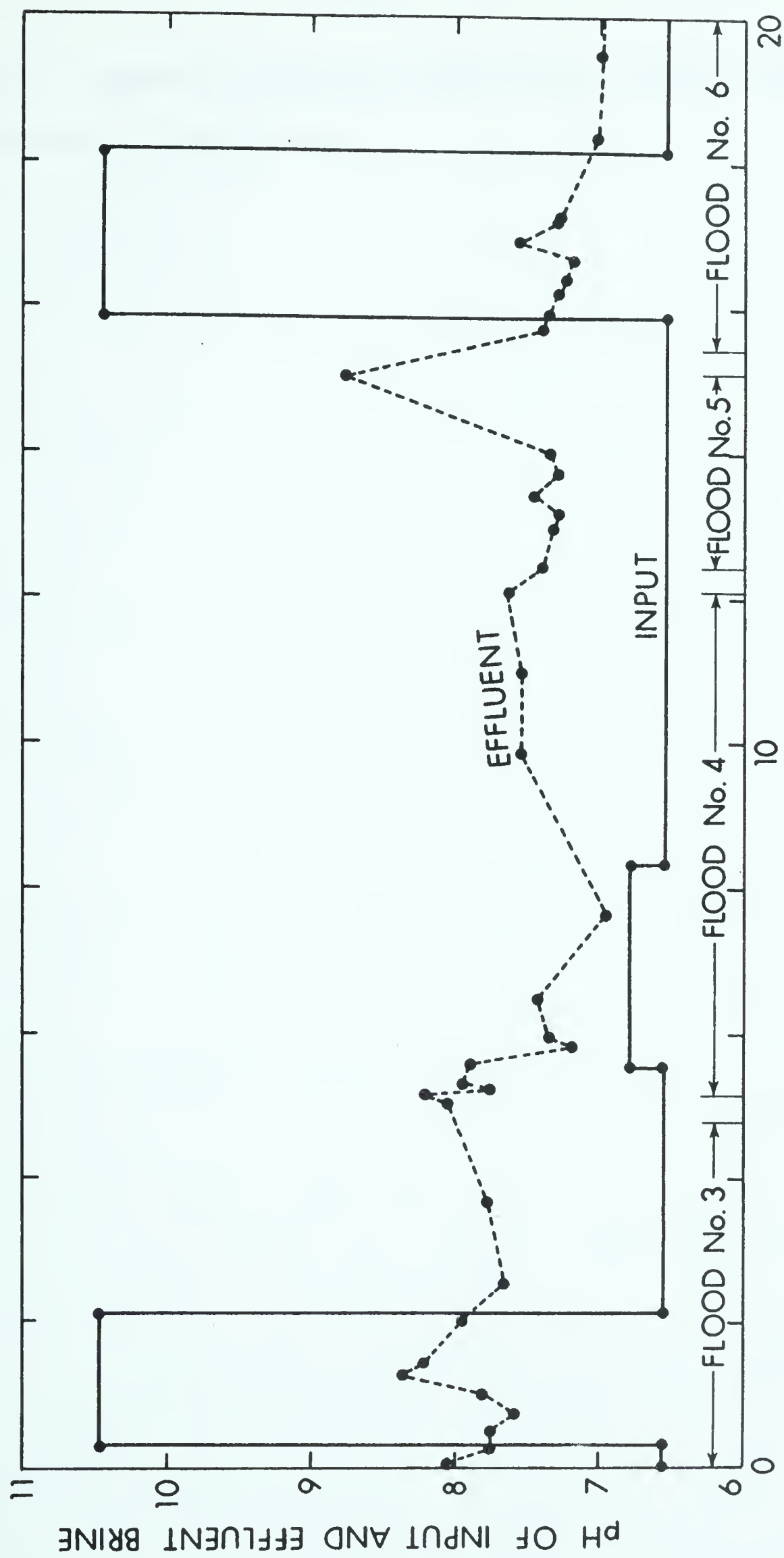
Figure 15 shows the pH of the input and effluent from the core model. There was chromatographic retention of NaOH in the core system as evidenced by the relationship of the input and effluent pH. Although the effluent pH rises above the brine level it does not at any time reach the high value of the input.

Consideration must also be given to the possibility of permanent adsorption on the sand grains. Timmins and Michaels(88) have established the adsorption for a number of chemicals including several of the amines. Some adsorption of NaOH would be expected, however, this adsorption may be fully or partially reversible.

Investigators as early as Nutting(72) have suggested that NaOH forms a compound with silica. The field test described by Leach et al(59) found a highly caustic silicate in the water produced. No specific study was made of adsorption or chemical reaction of NaOH in this work.

Sodium Hydroxide and Natural Oil Field Brine

Sodium hydroxide was added to a number of samples of natural brine. In each case a precipitate formed immediately after the addition of the NaOH. It is possible that this precipitate was calcium carbonate or magnesium



VARIATION OF EFFLUENT pH WITH SODIUM HYDOXIDE INJECTION

FIG: 15

hydroxide. Appendix D contains additional comments and data related to this problem.

CONCLUSIONS

The following conclusions may be made as a result of this experimental investigation into the effect of chemicals on water flood recovery of viscous crude oils.

1. All of the acid and alkali solutions tested reduced the interfacial tension between brine and Lloydminster, Chauvin and Swan Hills crude oils.

2. The alkali solutions appear more effective on the asphaltic crudes while the acids were slightly more effective in reducing the interfacial tension of paraffinic crude oils.

3. Alkali concentrations of 0.005 percent by weight were sufficient to reduce the interfacial tension of Lloydminster and Chauvin crude below 2 dynes per centimeter.

4. Filtering the Chauvin and Lloydminster crude oils through activated alumina did not significantly change the interfacial tension results.

5. The core sand sample used was sensitive to brine and the permeability decreased with time. Considering the large fraction of fine material in the sample, this reduction may be due to clay swelling.

6. The original core sand was probably slightly oil wet or neutral in wettability.

7. Natural or cleaned crude oil from Lloydminster emulsifies very easily with water and forms a comparatively stable emulsion which is difficult to break.

8. Weak sodium hydroxide solutions increased core model oil recoveries by 30 percent on the system studied.

9. Breakthrough recovery on the initial sodium hydroxide test was almost the same as the breakthrough recoveries of previous plain brine floods.

10. The wettability of the core model shifted towards the water wet side after contact with sodium hydroxide.

11. Improvements in injectivity expected with the use of sodium hydroxide were not clearly indicated.

12. There was some chromatographic retention of sodium hydroxide in the core system.

13. Sodium hydroxide forms a precipitate when added to a number of natural brines.

RECOMMENDATIONS

The interfacial tension data presented in this work was obtained at atmospheric pressure and may not be directly applicable to reservoir conditions. Hocott(45) found that oil-water interfacial tension increased slightly under pressure. Consideration of pressure should be made when applying this data.

Laboratory results of these displacement tests cannot be applied directly to field use. Before a sodium hydroxide flood could be performed in the field, it would be necessary to establish the effect of reservoir stratification and variations in permeability. A pattern water flood test may be warranted to determine the sweep efficiency of any flood pattern used. Additional investigation is necessary to determine the precipitate formed when sodium hydroxide is added to native brine and to find a method of eliminating this problem. The amount of chemical agent adsorbed on the sand should be established.

This work could be confirmed and extended to find the general characteristics of sodium hydroxide floods. It is recommended that small cores be used for the general data and that long core tests be used to confirm these results. A very stable emulsion of brine and crude oil is produced from the core. Stoppered, graduated containers suitable for centrifuging would allow heating and centrifuging to be done

without loss of any of the recovered fluids.

Artificial brine for core systems with a clay fraction could contain some bivalent ions such as magnesium or calcium. These ions inhibit the swelling of clays and may minimize any change in permeability.

The scaling problem evident when using viscous crude oils may be resolved by using a very long core system and flooding at very low rates.

LIST OF SYMBOLS

"A"	-	activated alumina filtered
API	-	American Petroleum Institute
ASTM	-	American Society for Testing Materials
BS & W	-	bottom sediment and water
BT	-	breakthrough
C	-	Choukes scaling factor
cc	-	cubic centimeter
cp	-	centipoise
°F	-	Fahrenheit degrees
f_w	-	fraction of water flowing
f_o	-	fraction of oil flowing
gm	-	gram
GOR	-	gas-oil ratio
I	-	de Haan's scaling factor
IOIP	-	initial oil in place
K,k	-	permeability
k_w	-	permeability to water
k_o	-	permeability to oil
L	-	length
ml	-	millilitre
"N"	-	natural crude oil
N_p	-	oil produced
ΔN_p	-	increment of oil produced
ΔP	-	pressure drop

ΔP_i	- initial pressure drop
PPM	- parts per million
PV	- pore volume
S_{wa}	- average water saturation
S_{wc}	- critical water saturation
S_{wd}	- downstream water saturation
μ_o	- oil viscosity
μ_w	- water viscosity
V	- superficial flood velocity
W_i	- water injected
WOR	- water oil ratio
W_p	- water produced
ΔW_p	- increment of water produced
λ_m	- mean finger distance
γ	- interfacial tension
γ_{IT}	- interfacial tension
γ_{ITo}	- interfacial tension originally
θ	- contact angle

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A P P E N D I X A
BASIC DATA

TABLE A-1

Core Sand Sample Properties

Sparky Sand - Aberfeldy A-8-30

Composite sample from 1714' to 1720' used for core packing.

U.S. Mesh	Aperture Diameter (millimeters)	Weight percent Retained
60	0.250	3.47
80	0.177	12.23
100	0.149	26.20
120	0.125	26.43
140	0.105	11.6
200	0.074	9.07
-200		11.05

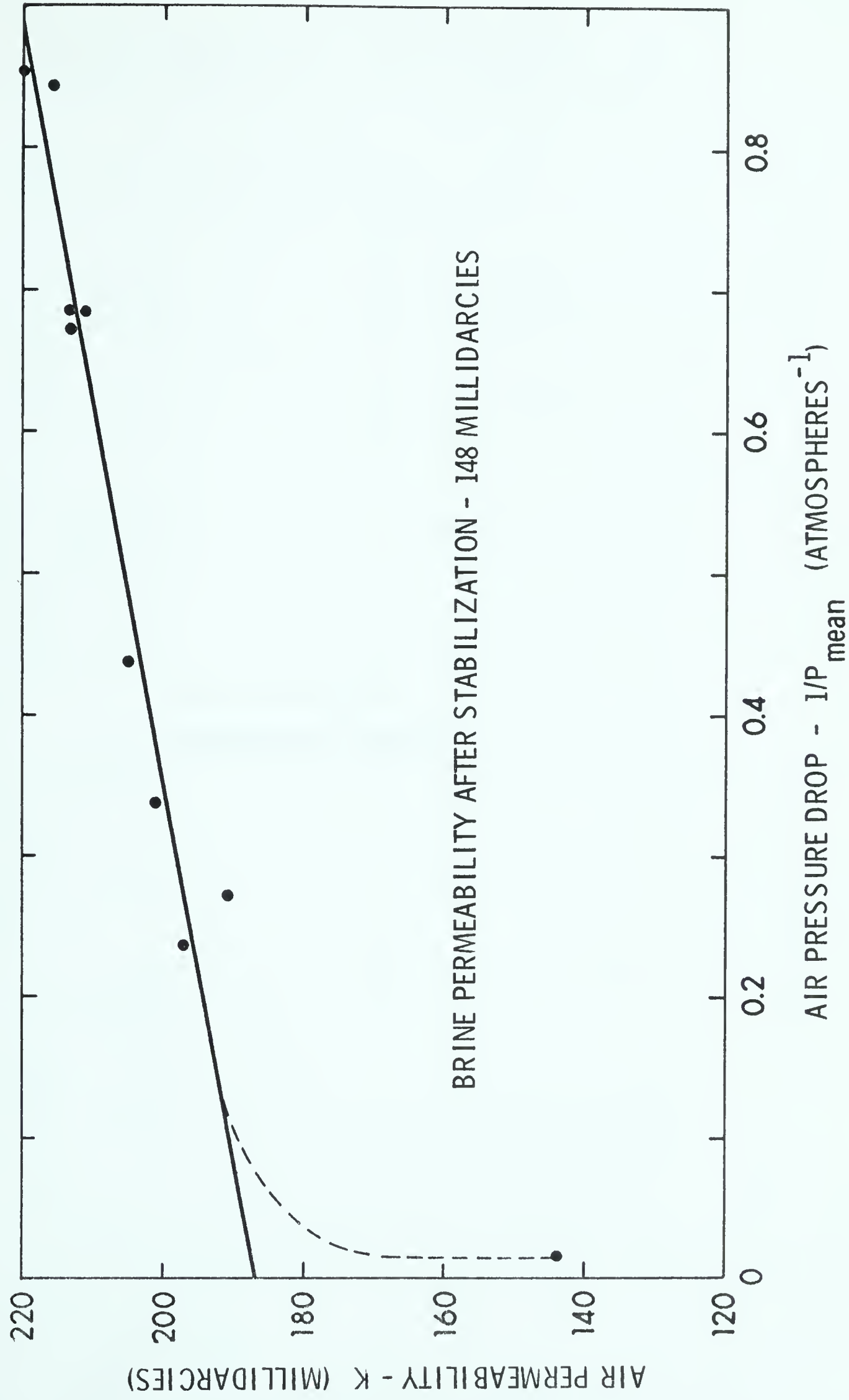


Figure A-1 KLINKENBERG AIR PERMEABILITY OF THE ARTIFICIAL CORE PACK

A P P E N D I X B
INTERFACIAL TENSION

TABLE B-1

Interfacial Tension Data - Sodium Hydroxide Solutions

Temperature = 80°F

Interfacial Tension (dynes/cm)

Solution Concentration Wt. % in Brine	pH	Interfacial Tension (dynes/cm)								Swan Hills "N"	
		Lloyd "N"		Lloyd "A"		Chauvin "N"		Chauvin "A"		$\frac{\gamma_{IT}}{\gamma_{ITO}}$	$\frac{\gamma_{IT}}{\gamma_{ITO}}$
		γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$		
5	11.8	<0.4	0.01	<0.4	0.01	<0.4	0.02	<0.4	0.02	8.0	0.29
0.5	11.7									14.3	0.53
0.05	11.2									18.1	0.67
0.01	10.68									-	
0.005	10.45	<0.4	0.01	<0.4	0.01	<0.4	0.02	<0.4	0.02	21.2	0.78
0.001	9.4	1.8	0.06	0.9	0.03	1.7	0.07	3.0	0.12	-	
0.0005	9.35	8.7	0.29	5.3	0.18	7.9	0.34	8.0	0.33	23.2	0.85
0.00025	7.84	28.2	0.95	23.0	0.77	21.7	0.93	21.2	0.88	-	
0.0001	6.78	28.3	0.96	27.6	0.93	22.8	0.98	22.5	0.93	-	
0	6.55	29.6	1.00	29.8	1.00	23.3	1.00	24.1	1.00	27.2	1.00

TABLE B-2

Interfacial Tension Data - Potassium Hydroxide Solution

Temperature = 80°F Solution Concentration Wt. % in Brine	pH	Interfacial Tension (dynes/cm)							
		Lloyd "N"		Lloyd "A"		Chauvin "N"		Chauvin "A"	
		γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$
5		<1.0	0.03	<2.0	0.07	<1.0	0.04	<1.0	0.04
0.5	11.85	16.2	0.55	4.6	0.15	15.1	0.65	11.3	0.47
0.05	11.1	23.5	0.79	10.4	0.35	18.0	0.77	16.5	0.68
0.01	10.5	27.0	0.91	28.0	0.94	22.3	0.96	22.6	0.94
0.005	10.2	29.6	1.00	29.8	1.00	23.3	1.00	24.1	1.00
0.001	9.2								
0.0005	8.85								
0.0001	6.8								
0	6.55								

5

11.85

11.1

10.5

10.2

9.2

8.85

6.8

6.55

9.3

10.3

17.1

21.9

21.1

25.5

26.7

26.7

27.2

0.34

0.38

0.63

0.81

0.78

0.94

0.98

0.98

1.00

1
83
1

TABLE B-3

Interfacial Tension Data - Sulphuric Acid Solutions

Temperature = 80°F		<u>Interfacial Tension (dynes/cm)</u>											
Solution Concentration Wt. % in Brine	pH	Lloyd "N"		Lloyd "A"		Chauvin "N"		Chauvin "A"		Swan Hills "N"			
		γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$		
5	0.17	13.1	0.44	13.0	0.44	12.0	0.52	12.5	0.52	5.4	0.20		
0.5	0.9	17.8	0.60	17.4	0.58	16.4	0.70	16.5	0.68	5.9	0.22		
0.05	1.8	20.8	0.70	21.3	0.71	19.3	0.83	19.3	0.76	9.2	0.34		
0.005	2.8	24.9	0.84	24.1	0.81	21.3	0.91	22.1	0.92	11.6	0.43		
0.0005	4.1	29.6	1.00	28.9	0.97	23.8	1.02	24.2	1.00	19.4	0.71		
S _w	6.55	29.6	1.00	29.8	1.00	23.3	1.00	24.1	1.00	27.2	1.00		

1 84 1

TABLE B-4

Interfacial Tension Data - Concentrated Solutions of Acids and Bases

Temperature = 80°F		Interfacial Tension (dynes/cm)											
Solution Concentration Wt. % in Brine	pH	Lloyd "N"		Lloyd "A"		Chauvin "N"		Chauvin "A"		Swan Hills "N"			
		γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$	γ_{IT}	$\frac{\gamma_{IT}}{\gamma_{ITO}}$
5% NaOH	11.8	4.0	0.03	1.0	0.03	1.0	0.04	1.0	0.04	8.0	0.29		
5% KOH		1.0	0.03	1.0	0.03	1.0	0.04	1.0	0.04	9.3	0.34		
0.1 Ca(OH) ₂	11.35	13.5	0.46	13.6	0.46	11.6	0.50	11.7	0.49	19.7	0.72		
5% H ₂ SO ₄	0.17	13.1	0.44	13.0	0.44	12.0	0.52	12.5	0.52	5.4	0.20		
5% HCl	0	12.3	0.42	12.3	0.41	11.1	0.48	11.1	0.46	5.9	0.22		
5% Acetic Acid	2.2	20.7	0.70	20.7	0.69	19.2	0.82	19.4	0.80	10.1	0.37		
5% Citric Acid	1.45	18.2	0.61	18.2	0.61	17.9	0.77	18.5	0.77	8.6	0.32		

TABLE B-5

Surface Tension of Local Crude Oils

T = 80°F

Du Nouy Tensiometer Method

<u>Liquid</u>	<u>Density gm/ml</u>	<u>Surface Tension dynes/cm</u>
Lloydminster Natural Crude	0.9558	30.1
Lloydminster Alumina Filtered Crude	0.9560	31.4
Chauvin Natural Crude	0.9145	27.9
Chauvin Alumina Filtered Crude	0.9140	28.7
Swan Hills Natural Crude	0.8188	25.2
Artificial Brine (84.839 gm NaCl/litre)	1.05615	73.0

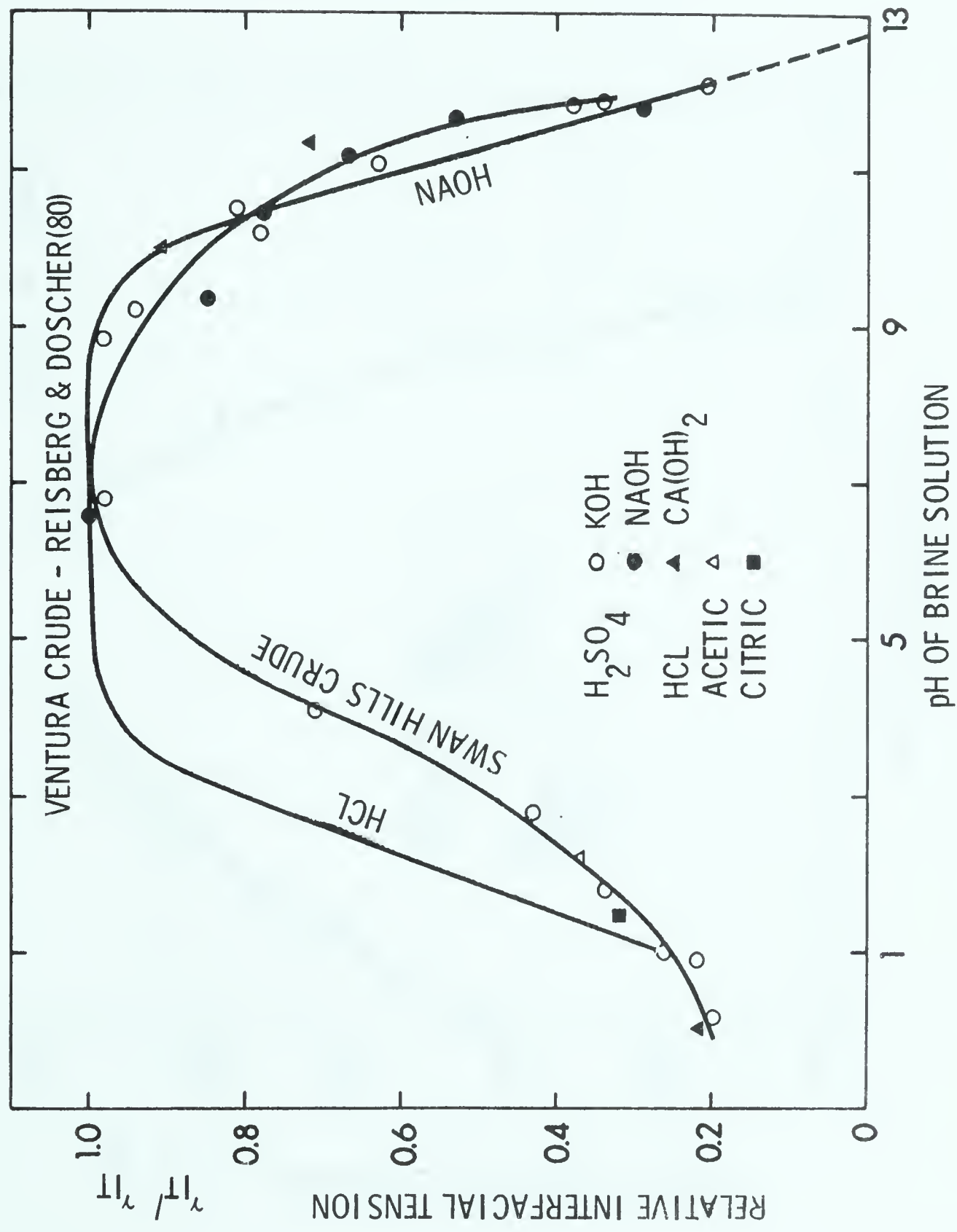


Figure B-1 EFFECT OF BRINE pH ON THE INTERFACIAL TENSION OF SWAN HILLS AND VENTURA CRUDE OIL

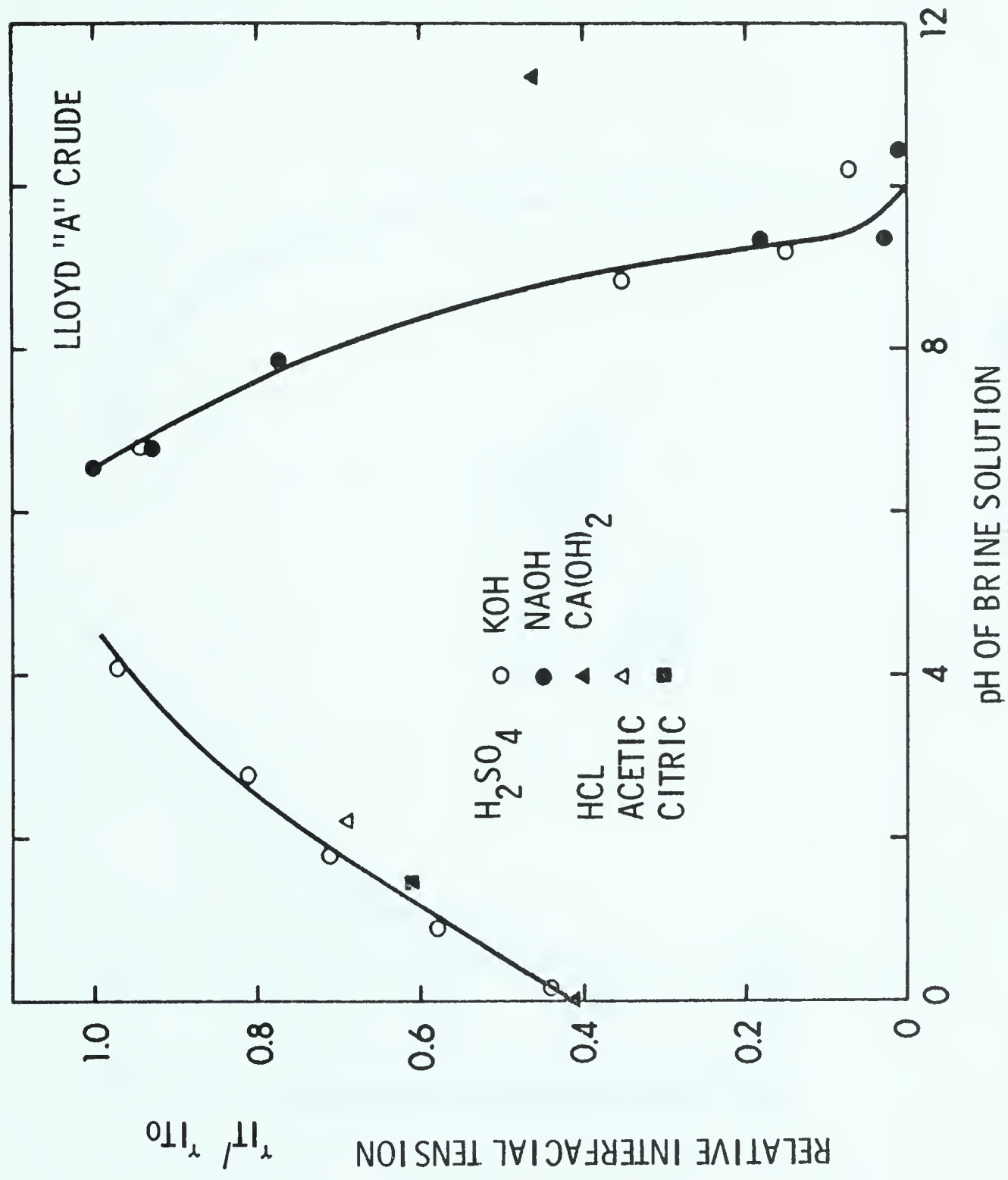


Figure B-2 EFFECT OF BRINE pH ON THE INTERFACIAL TENSION

OF ALUMINA FILTERED LLOYDMINSTER CRUDE OIL

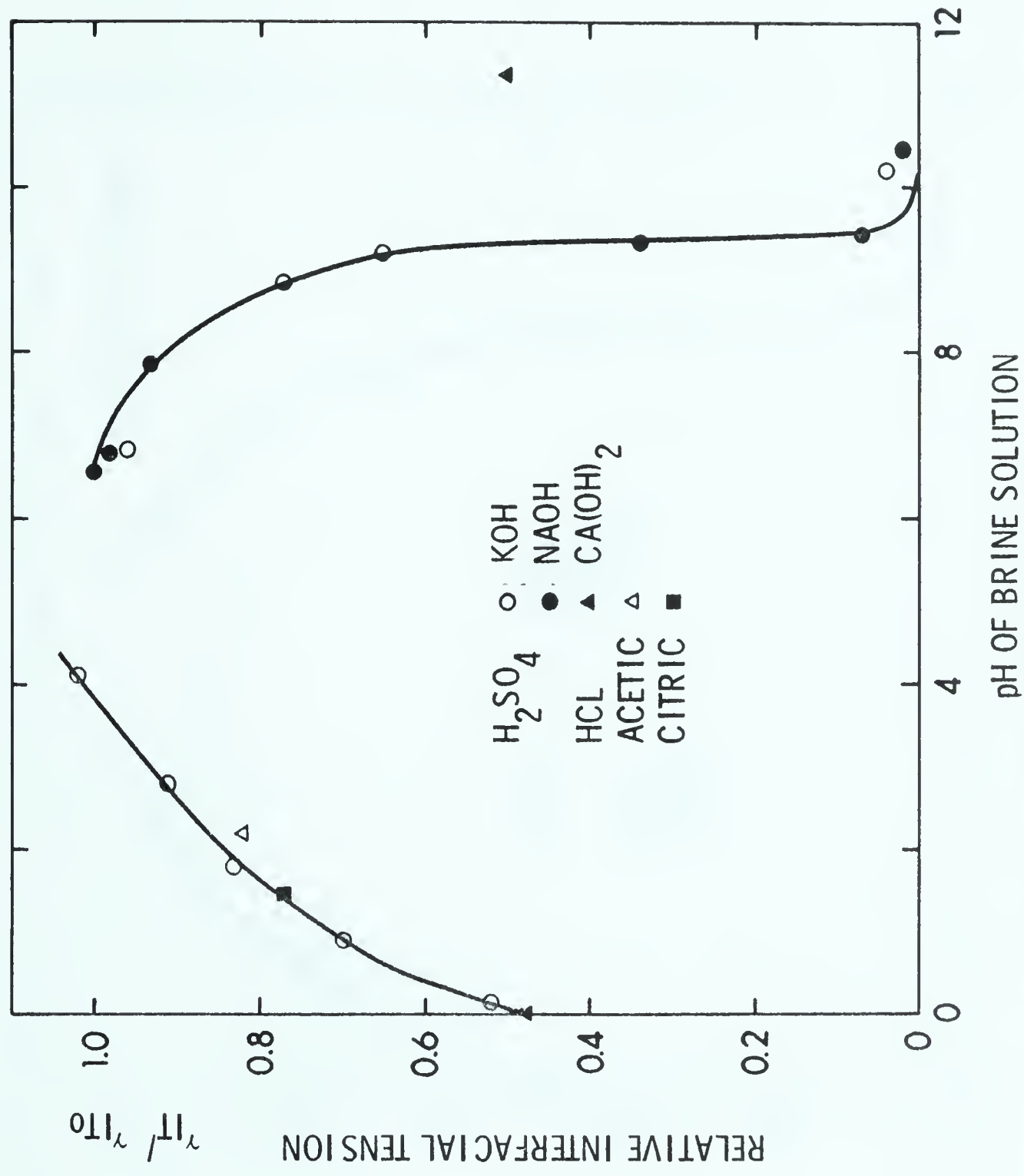


Figure B-3 EFFECT OF BRINE pH ON THE INTERFACIAL TENSION OF NATURAL CHAUVIN CRUDE OIL

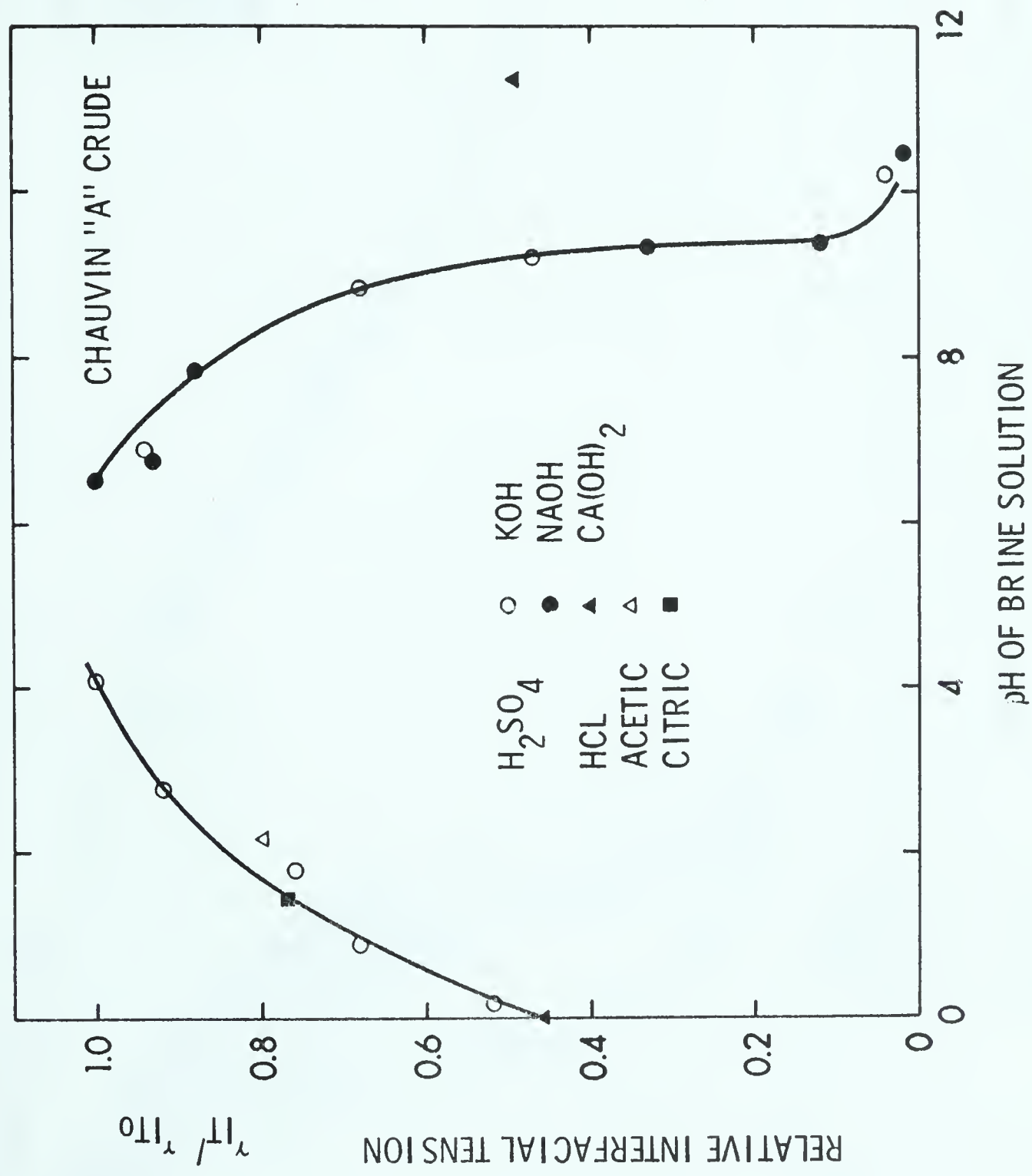


Figure B-4 EFFECT OF BRINE pH ON THE INTERFACIAL TENSION
OF ALUMINA FILTERED CHAUVIN CRUDE OIL

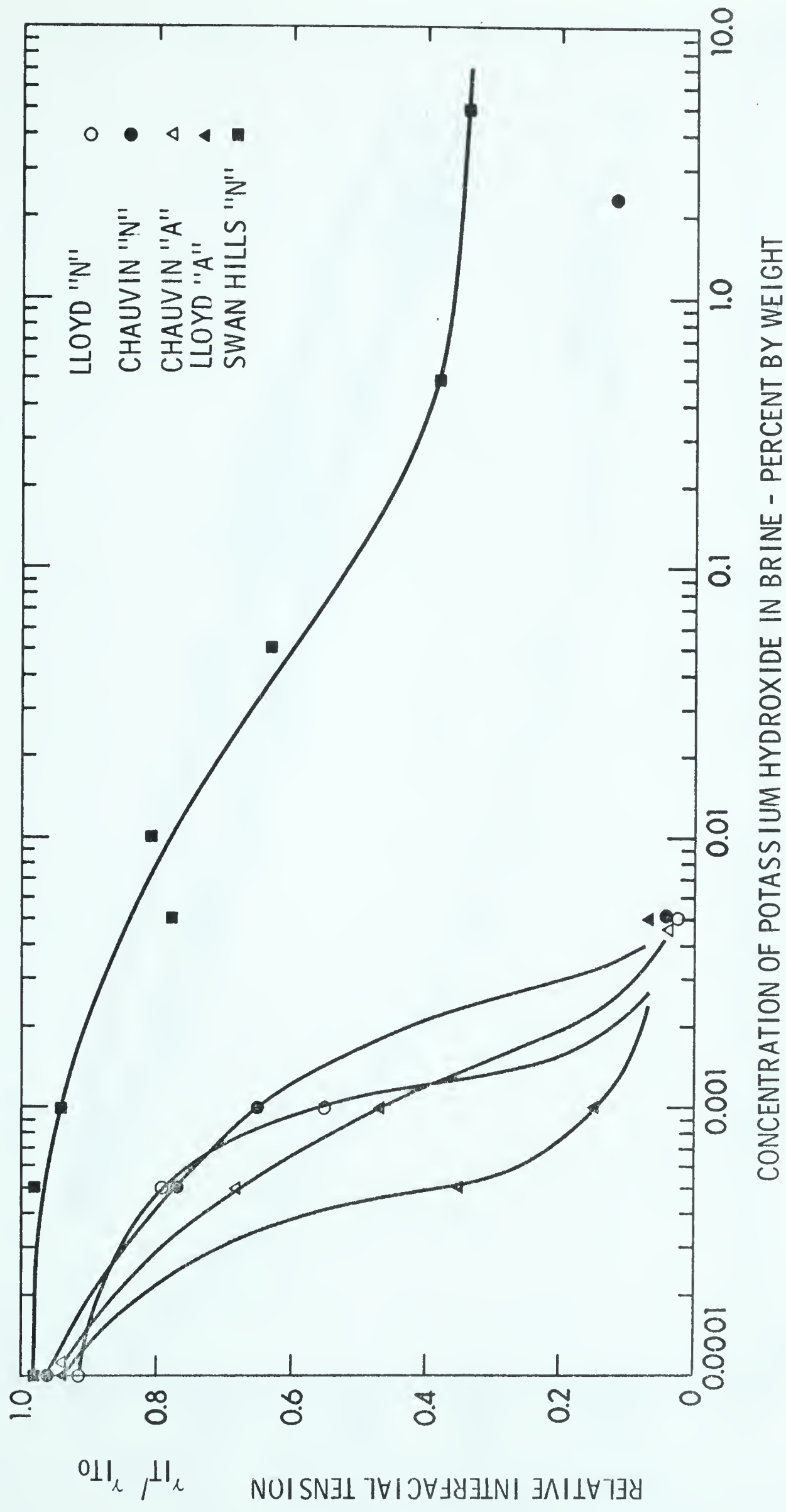
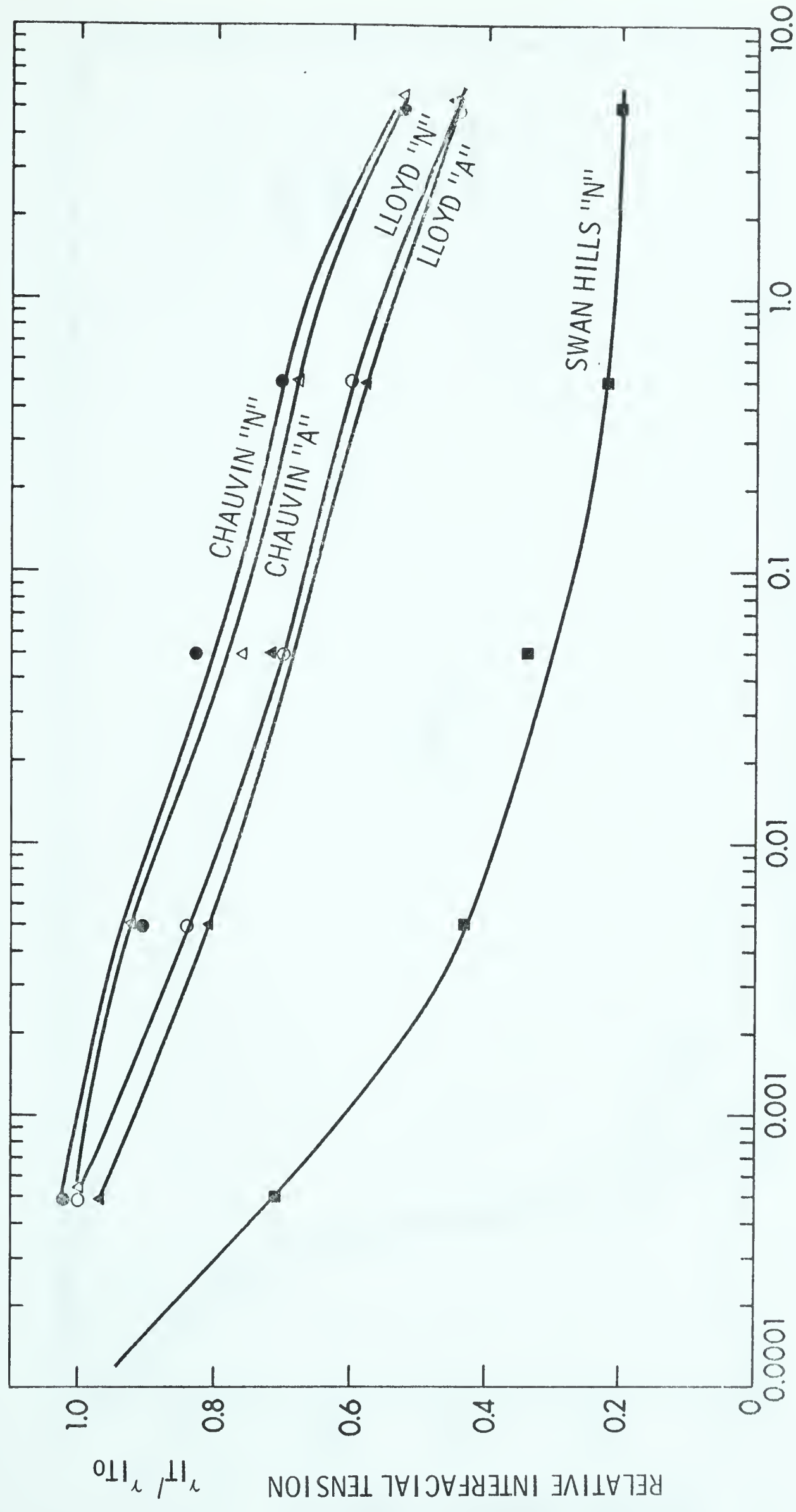


Figure B-5 EFFECT OF POTASSIUM HYDROXIDE CONCENTRATION ON THE
BRINE-CRUDE OIL INTERFACIAL TENSION OF LOCAL CRUDE OILS



CONCENTRATION OF SULPHURIC ACID IN BRINE - PERCENT BY WEIGHT

Figure B-6 EFFECT OF SULPHURIC ACID CONCENTRATION ON THE BRINE-CRUDE OIL

INTERFACIAL TENSION OF LOCAL CRUDE OILS

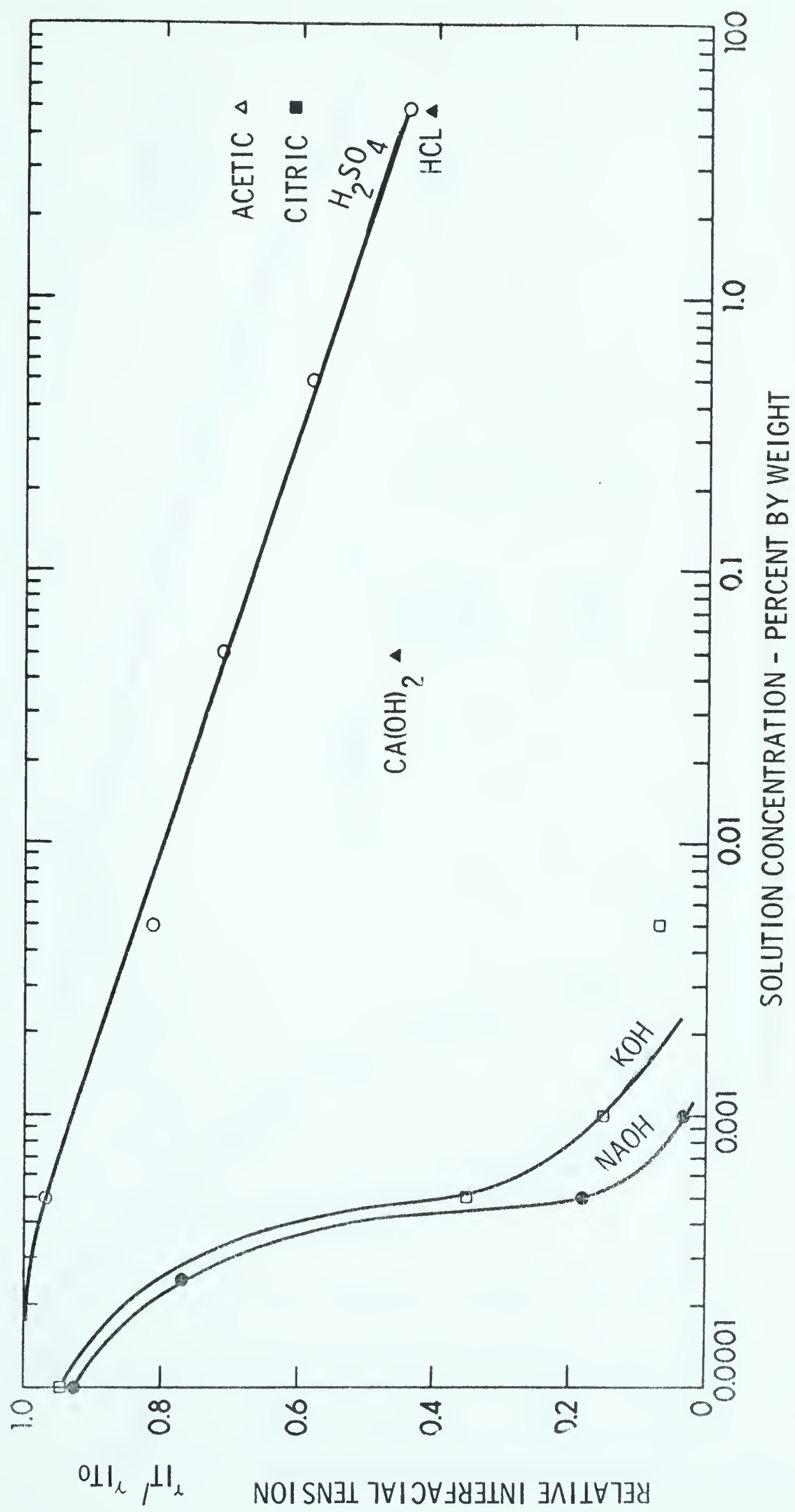


Figure B-7 INFLUENCE OF ACID AND ALKALI CONCENTRATION ON INTERFACIAL TENSION OF ALUMINA FILTERED LLOYDMINSTER CRUDE AND BRINE

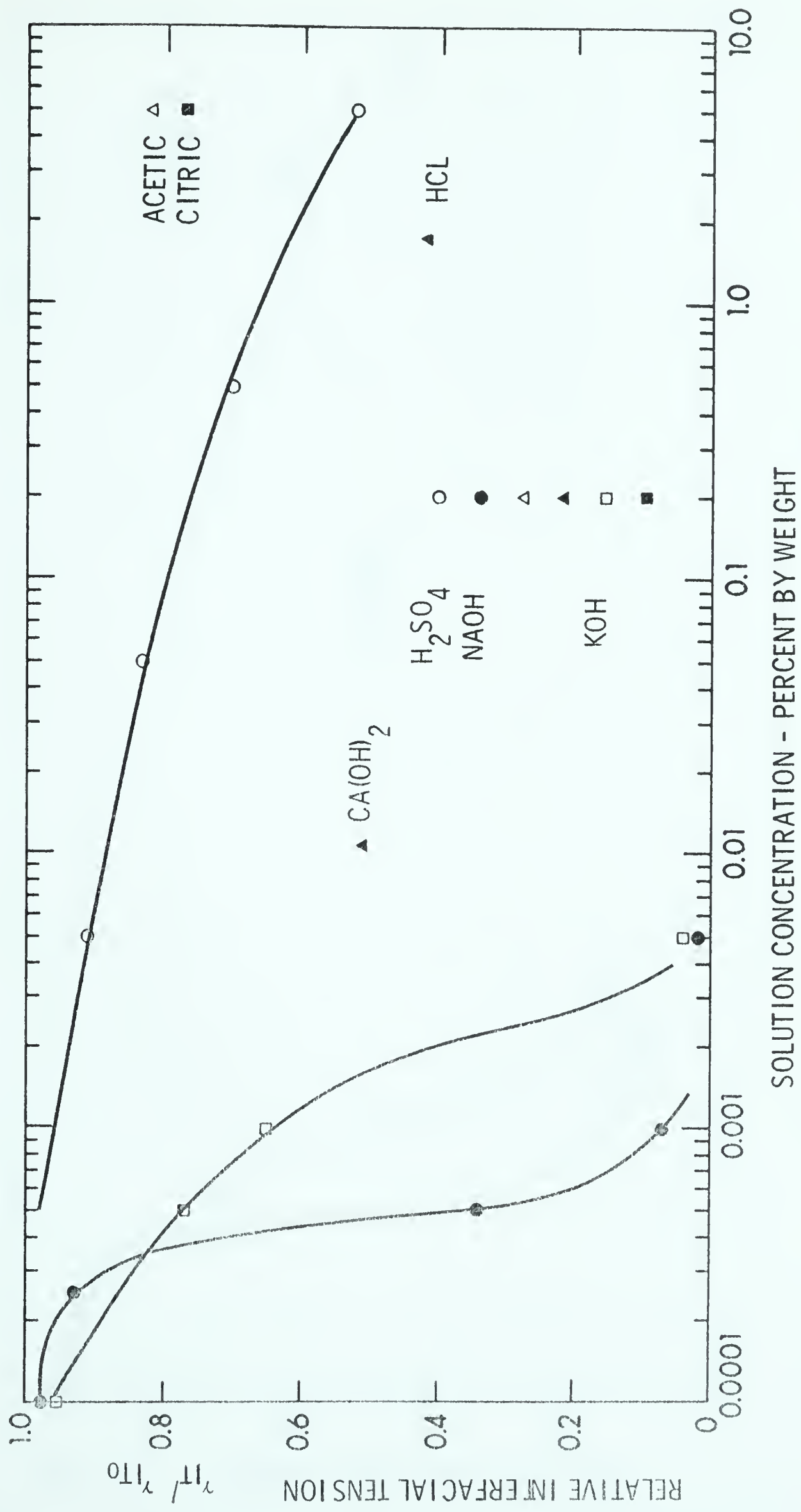


Figure B-8 INFLUENCE OF ACID AND ALKALI CONCENTRATION ON THE INTERFACIAL

TENSION OF NATURAL CHAUVIN CRUDE OIL AND BRINE

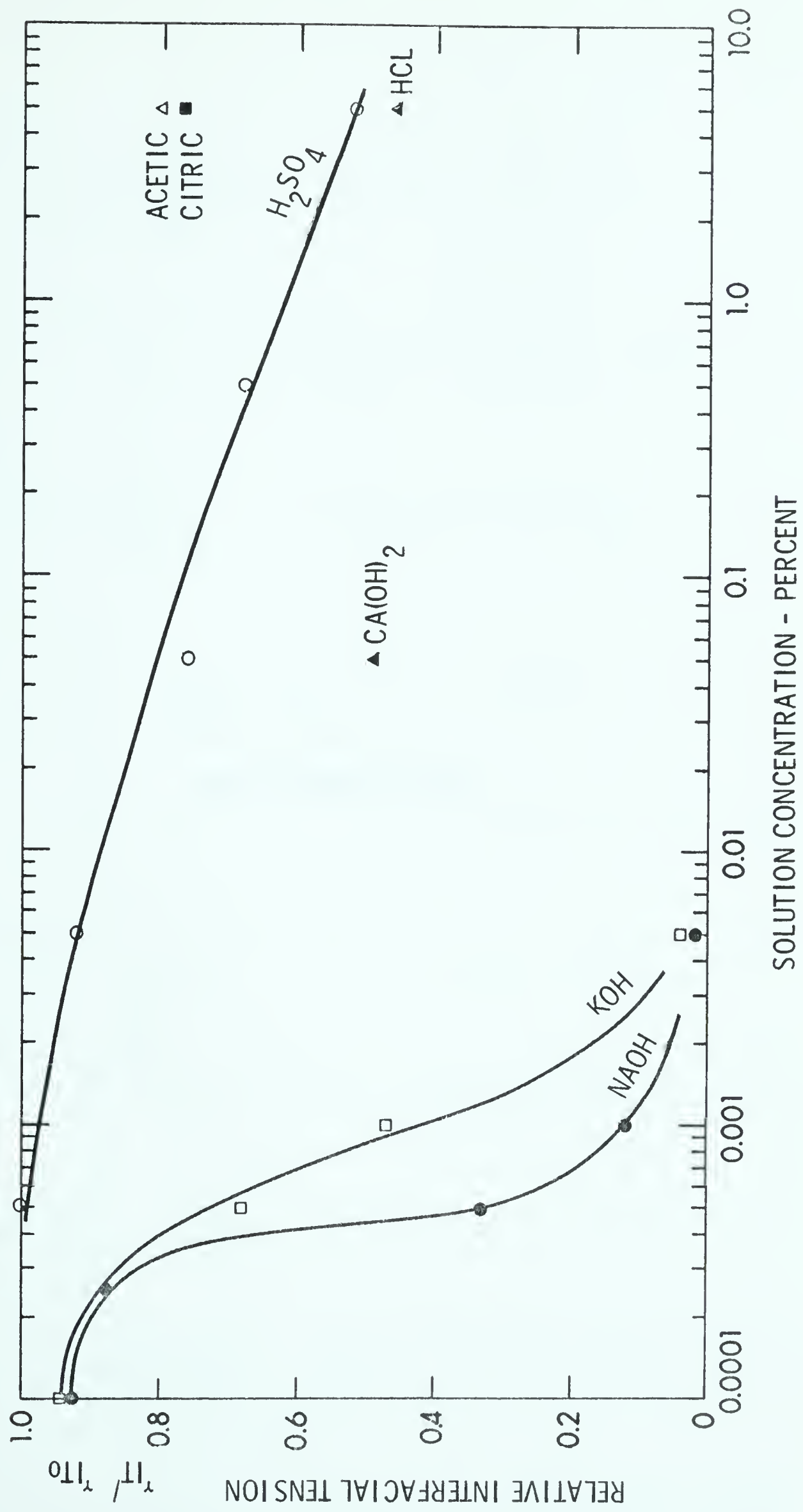


Figure B-9 INFLUENCE OF ACID AND ALKALI CONCENTRATION ON THE INTERFACIAL TENSION OF ALUMINA FILTERED CHAUVIN CRUDE OIL AND BRINE

A P P E N D I X C

DISPLACEMENT TESTS

TABLE C-1

Displacement Test Recovery Data - Test Number 1

Pore Volume - 890 cc		Temperature - 80°F	Oil - Alumina filtered Lloydminster crude						
Injected Phase - artificial brine		Displacement rate - 10.25 cc/hr	μ_w - 0.9934 cp						
$S_{wc} = 0.283$ (artificial brine)		Initial oil in place - 638 cc	μ_o - 1160 cp						
<u>Brine Injected</u>		<u>Recovery</u>		<u>Cumulative Oil</u>	<u>Pressure</u>				
W_i cc	W_i P.V.	ΔN_p cc	N_p cc	ΔW_p cc	W_p cc	Avg. WOR	IOIP	P.V.	Drop ΔP psi
0	0					0			709
38	0.043	41	41	0	0	1.0	0.064	0.046	508
221	0.248	90	131	93	93	4.8	0.205	0.147	131
444	0.499	39	170	186	279	9.5	0.266	0.191	97
942	1.059	47	217	447	726	13.6	0.340	0.244	73
1160	1.303	15	232	204	930	16.4	0.364	0.261	66
1404	1.577	14	246	230	1160	21.4	0.386	0.277	43
1628	1.829	10	256	214	1374	23.6	0.401	0.288	55
1898	2.133	11	267	260	1634	17.7	0.419	0.300	-
1943	2.184	3	270	53	1687		0.423	0.303	52

TABLE C-2

Displacement Test Recovery Data - Test Number 2

Pore Volume - 882 cc Temperature 80°F Oil - Alumina filtered Lloydminster crude
 Injected Phase - artificial brine Displacement rate - 10.25 cc/hr μ_w - 0.9934 cp
 $S_{wc} = 0.285$ (artificial brine) Initial oil in place - 630 cc μ_o - 1160 cp

Brine Injected		Recovery			Avg. WOR	Cumulative Oil			Pressure Drop ΔP
W_i cc	W_i P.V.	ΔN_p cc	N_p cc	ΔW_p cc		W_p cc	IOIP	P.V.	
0	0				0				1071
75	0.085	77	77	0		0	0.126	0.087	644
95	0.108	20	97	trace	B.T.	trace	0.153	0.110	588
115	0.130	16	113	5	0.3	5	0.178	0.128	534
162	0.184	18	131	26	1.4	31	0.207	0.149	416
249	0.282	24	155	59	2.5	90	0.245	0.176	286
459	0.520	41	196	169	4.1	259	0.310	0.222	223
563	0.638	16	212	88	5.5	347	0.335	0.240	205
641	0.727	8	220	72	9.0	419	0.347	0.249	182
711	0.807	8	228	62	7.8	481	0.360	0.259	167
832	0.943	9	237	93	10.3	574	0.374	0.269	162
1063	1.206	16	253	233	14.6	807	0.400	0.287	138
1323	1.499	14	267	246	17.6	1053	0.422	0.303	124
1571	1.781	12	279	236	19.7	1289	0.441	0.316	112
1842	2.088	6	285	265	14.2	1554	0.450	0.323	102
1918	2.175	2	287	75	37.5	1629	0.453	0.325	98

TABLE C-3

Displacement Test Recovery Data - Test Number 3

Pore Volume - 882 cc Temperature - 80°F Oil - Alumina filtered Lloydminster crude
 Injected Phase - 0.005% by wt. NaOH in artificial brine Displacement rate - 10.25 cc/hr
 $S_{wc} = 0.309$ (artificial brine) Initial Oil in Place - 609 cc $\mu_o = 1160$ cp $\mu_w = 0.9934$ cp

<u>Brine Injected</u>			<u>Recovery</u>			Avg. WOR	<u>Cumulative Oil</u>		Pressure Drop ΔP psi
W_i cc	W_i P.V.	ΔN_p cc	N_p cc	ΔW_p cc	W_p cc		IOIP	P.V.	
0	0					0			989
94	0.107	93	93	1	1		0.153	0.105	632
181	0.205	52	145	32	33	0.6	0.238	0.164	474
230	0.261	33	178	21	54	0.6	0.292	0.202	-
485	0.550	90	268	164	218	1.8	0.440	0.304	167
738	0.836	30	298	225	443	7.5	0.489	0.338	126
981	1.112	20	318	230	673	11.5	0.522	0.361	-
1233	1.398	15	333	233	906	15.5	0.547	0.378	-
1472	1.669	11	344	229	1135	20.8	0.565	0.390	-
1622	1.839	7	351	143	1278	20.4	0.576	0.398	-
2168	2.458	19	370	520	1798	27.4	0.607	0.420	74
2625	2.976	14	384	248	2246	17.7	0.630	0.435	63
3625	4.109	16	400	989	3235	61.8	0.656	0.454	58
4625	5.243	5	405	995	4230	199.0	0.665	0.459	-

TABLE C-4

Displacement Test Recovery Data - Test Number 4

Pore Volume - 882 cc Temperature - 80°F Oil - Alumina filtered Lloydminster crude
 Injected Phase - 0.0001% by wt. NaOH in artificial brine Displacement rate - 10.25 cc/hr
 $S_{wc} = 0.392$ (artificial brine) Initial Oil in Place - 536 cc $\mu_o = 1160$ cp $\mu_w = 0.9934$ cp

<u>Brine Injected</u>		<u>Recovery</u>			Avg. WOR	<u>Cumulative Oil</u>		Pressure Drop ΔP psi
W_i cc	W_i P.V.	ΔN_p cc	N_p cc	ΔW_p cc		Recovery IOIP	P.V.	
0	0							1216
100	0.113	100	100	0	0	0.186	0.113	-
246	0.279	86	186	66	0.8	0.347	0.210	581
358	0.406	21	207	86	6.2	0.386	0.235	357
623	0.707	37	244	229	12.2	0.455	0.277	354
859	0.974	18	262	220	17.0	0.489	0.297	200
966	1.095	6	268	102	20.9	0.500	0.304	182
1466	1.662	23	291	480	57.9	0.543	0.330	139
2468	2.80	17	308	985	51.5	0.574	0.349	-
3468	3.94	19	327	978	99.2	0.610	0.371	-
4468	5.07	10	337	992	110.4	0.628	0.382	
5468	6.21	9	346	994	199.8	0.645	0.392	-
6468	7.34	5	351	999		0.654	0.398	53

TABLE C-5

Displacement Test Recovery Data - Test Number 5

Pore Volume - 882 cc Temperature - 80°F Oil - Alumina filtered Lloydminster crude
 Injected Phase - artificial brine Displacement rate - 10.25 cc/hr $\mu_o = 1160$ cp
 $S_{wc} = 0.451$ (artificial brine) Initial oil in place - 484 cc $\mu_w = 0.9934$ cp

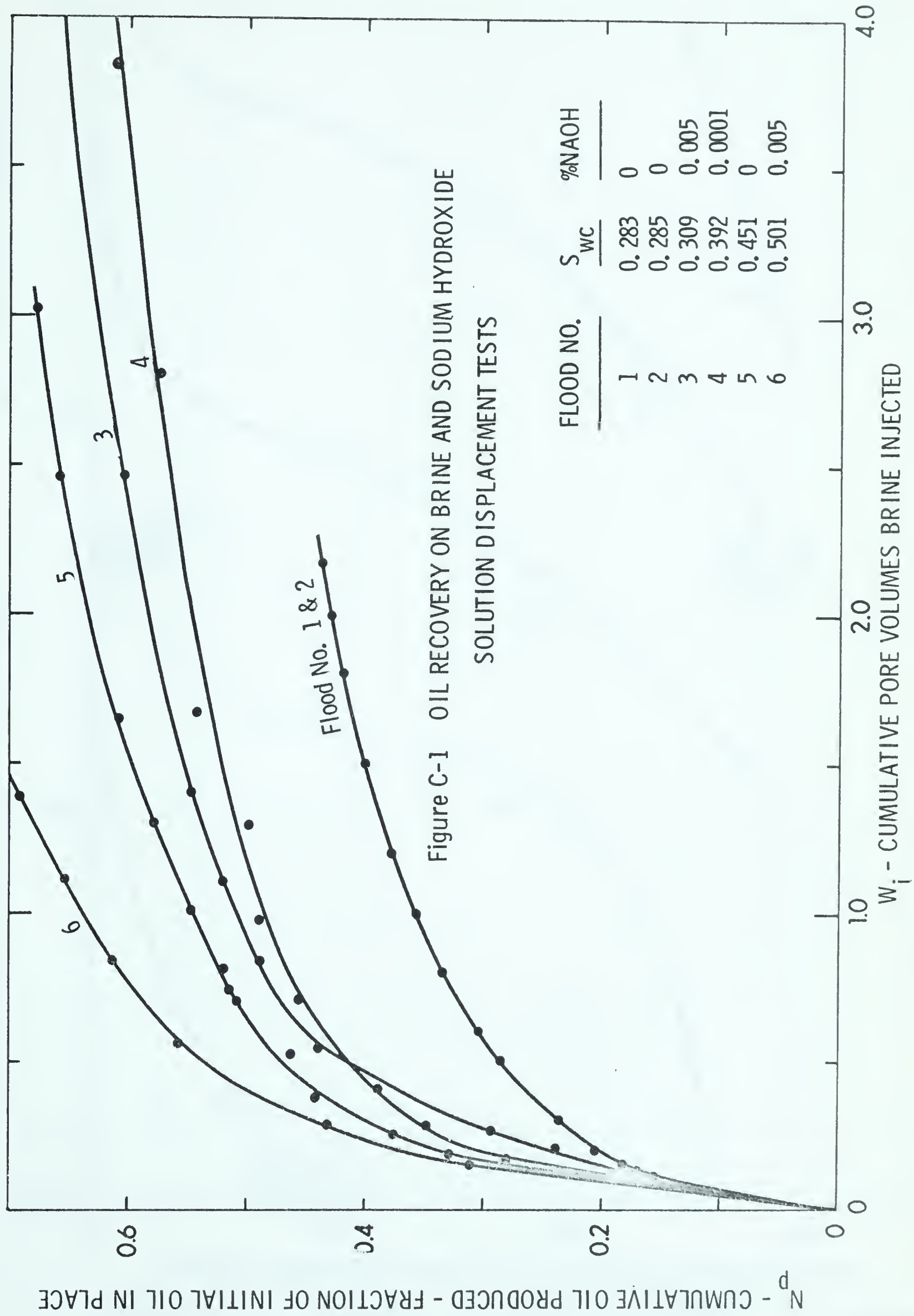
<u>Brine Injected</u>		<u>Recovery</u>			Wp cc	Avg. WOR	<u>Cumulative Oil</u>		Pressure Drop ΔP psi
Wi cc	Wi P.V.	ΔN_p cc	Np cc	ΔW_p cc			Recovery IOIP	P.V.	
0	0					0			1151
160	0.181	159	159	0	0	1.5	0.328	0.180	525
224	0.254	23	182	34	34	2.3	0.376	0.206	374
330	0.375	33	215	76	110	14.0	0.444	0.244	257
467	0.529	9	224	126	236	6.3	0.462	0.254	201
621	0.704	22	246	138	374	9.0	0.508	0.279	174
653	0.470	3	249	27	401	19.0	0.514	0.282	172
716	0.812	3	252	57	458	12.3	0.520	0.286	-
890	1.009	13	265	160	618	15.9	0.547	0.300	139
1144	1.296	15	280	239	857	19.7	0.578	0.317	120
1453	1.648	15	295	295	1152	23.2	0.609	0.334	101
1671	1.895	9	304	209	1361	31.8	0.628	0.345	91
2162	2.451	15	319	477	1838	53.3	0.659	0.362	65
2654	3.009	9	328	480	2318		0.677	0.372	53

TABLE C-6

Displacement Test Recovery Data - Test Number 6

Pore Volume - 882 cc Temperature - 80°F Oil - Alumina filtered Lloydminster crude
 Injected Phase - 0.005% by wt. NaOH in artificial brine Displacement rate - 10.25 cc/hr
 $S_{wc} = 0.501$ (artificial brine) Initial oil in place - 536 cc $\mu_o = 1160$ cp $\mu_w = 0.9934$ cp

Brine Injected		Recovery			Avg. WOR	Cumulative Oil Recovery Fraction		Pressure Drop ΔP psi
W_i cc	W_i cc	ΔN_p cc	N_p cc	ΔW_p cc		IOIP	P.V.	
0	0							1143
100	0.113	100	100	0	0	0.229	0.113	-
248	0.281	87	187	57	0.7	0.429	0.212	357
497	0.563	55	242	193	3.5	0.555	0.274	225
739	0.838	25	267	217	8.7	0.612	0.303	177
984	1.116	18	285	228	12.7	0.654	0.323	145
1198	1.358	16	301	198	12.4	0.690	0.341	109
1486	1.685	22	323	229	10.4	0.741	0.366	99
1691	1.917	18	341	229	12.7	0.782	0.387	93
1928	2.186	13	354	226	17.4	0.812	0.401	83
1986	0.252	3	357	56	18.7	0.819	0.405	-
2988	3.388	23	380	975	42.4	0.872	0.431	63
3988	4.522	16	396	986	61.6	0.908	0.449	60



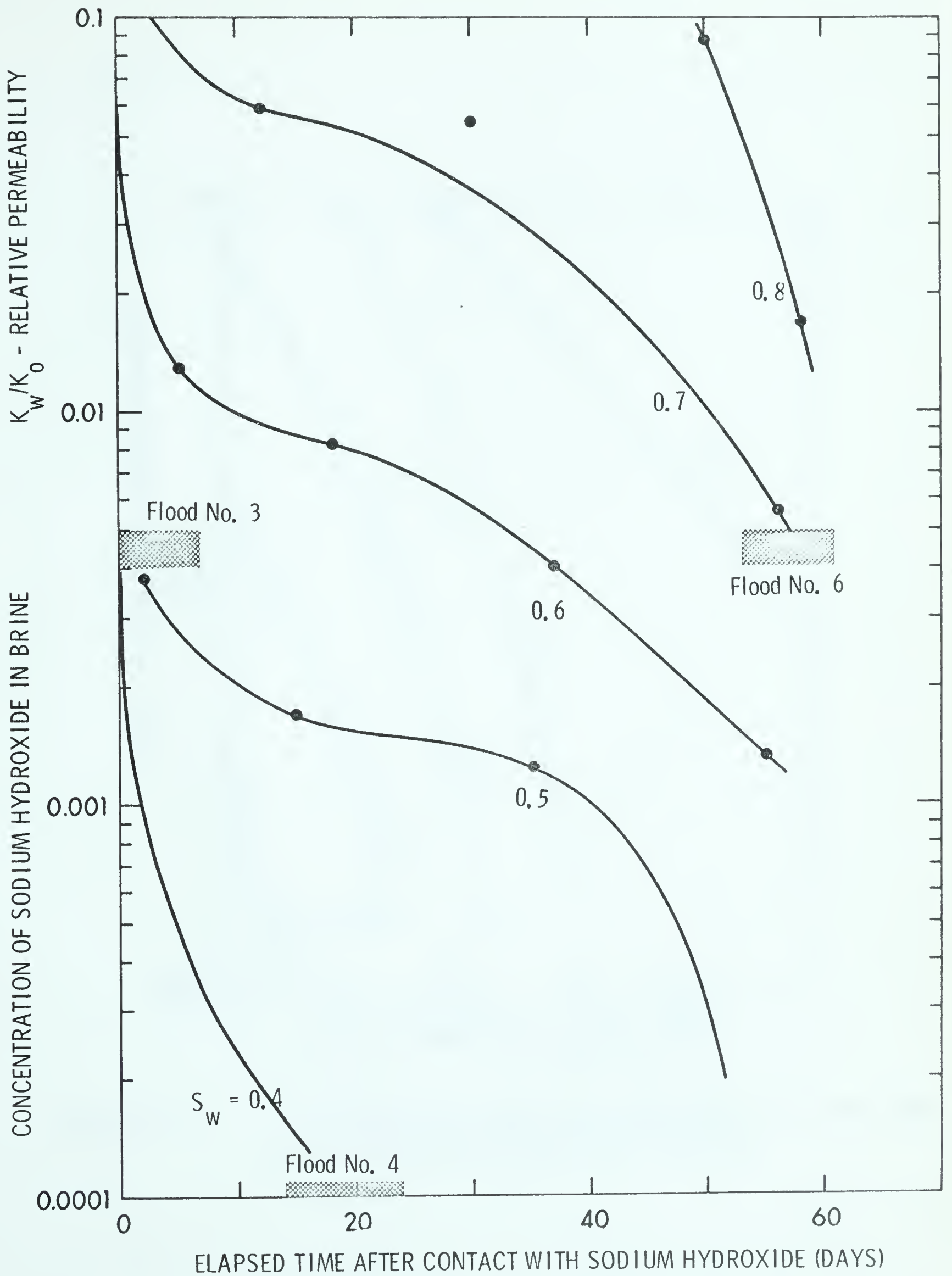


Figure C-2 CHANGE IN RELATIVE PERMEABILITY WITH SODIUM HYDROXIDE CONTACT TIME

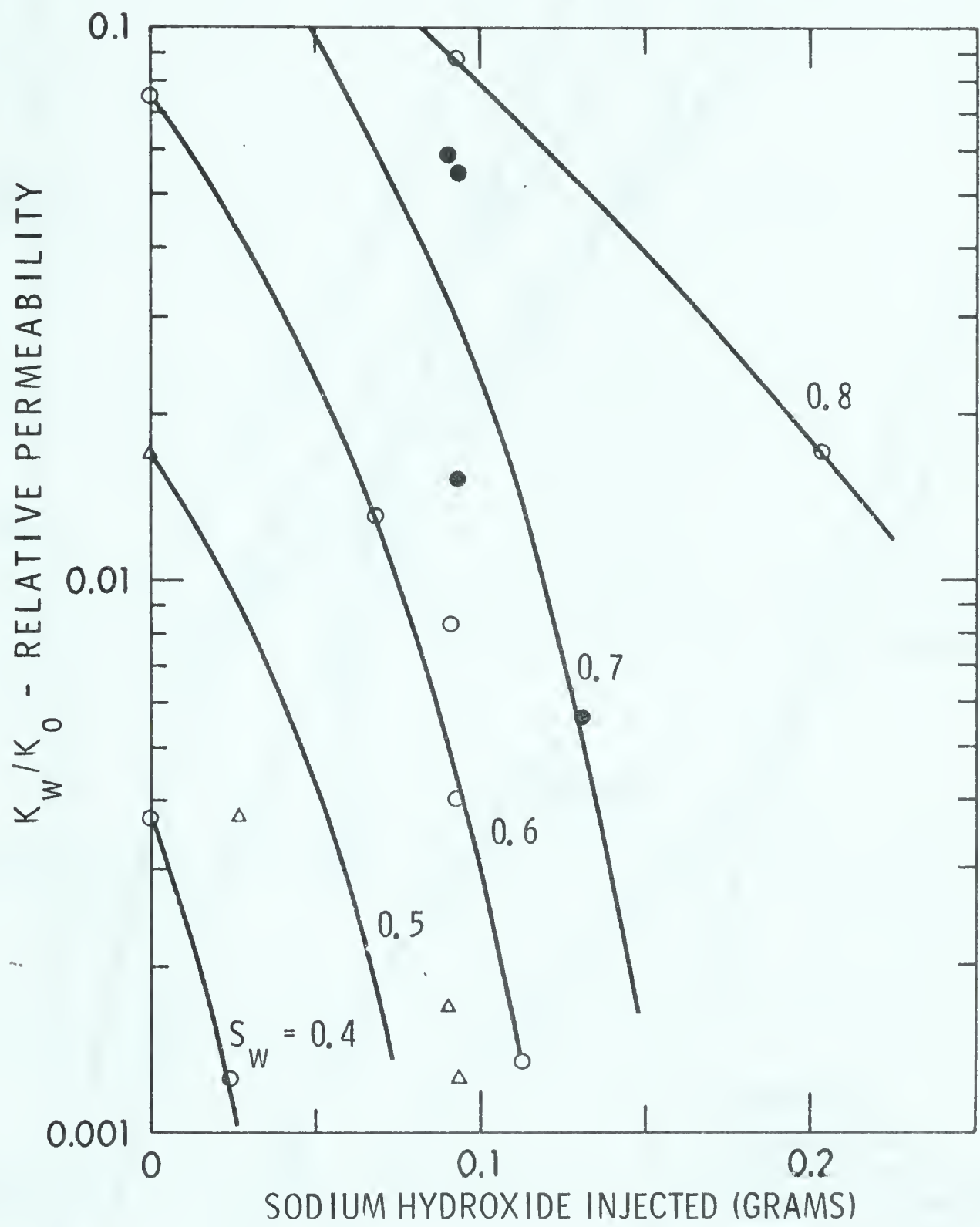


Figure C-3

CHANGE IN RELATIVE PERMEABILITY OF CORE
WITH SODIUM HYDROXIDE INJECTED

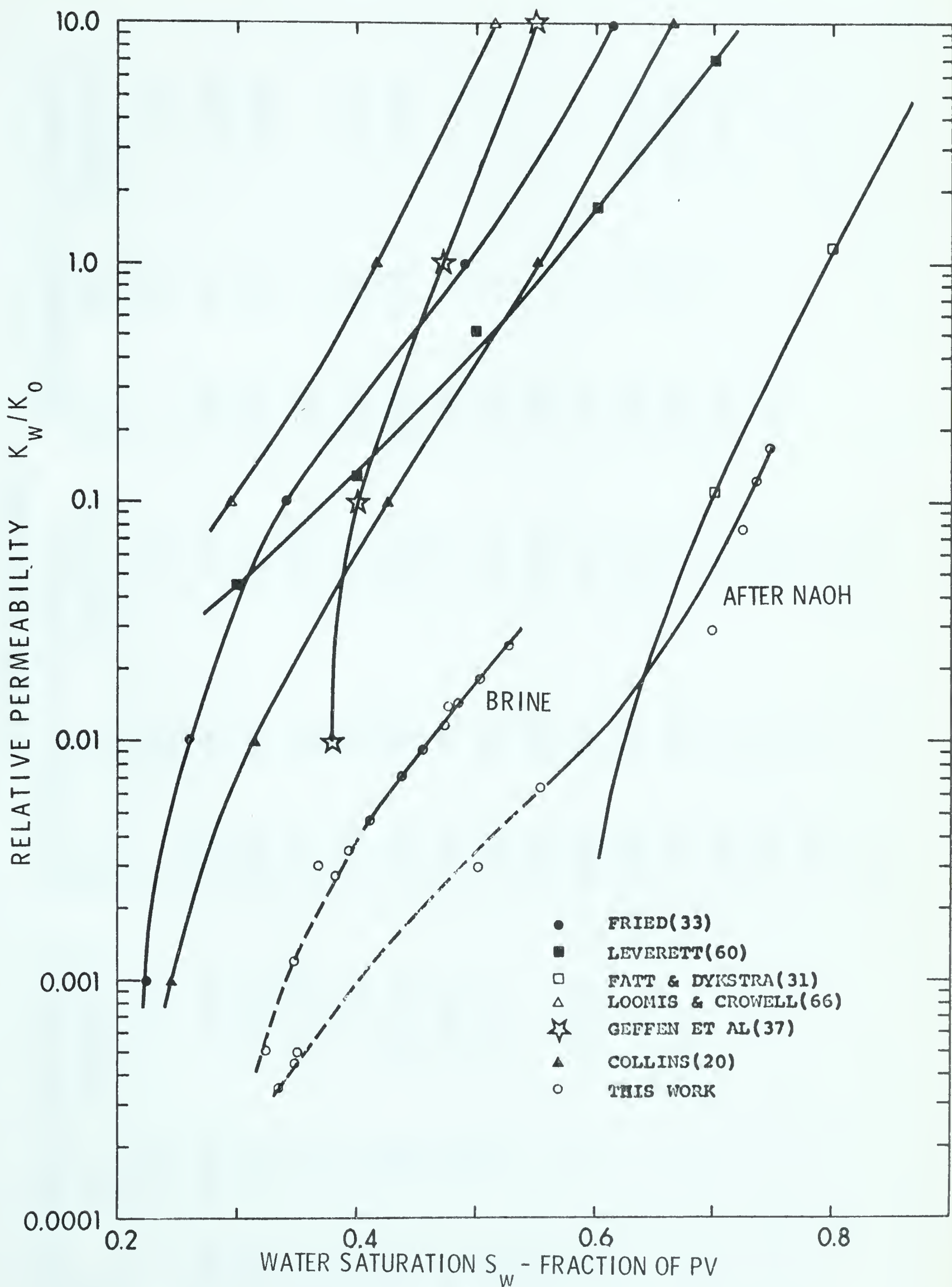


Figure C-4 RELATIVE PERMEABILITY COMPARISONS

TABLE C-7

Relative Injectivity

<u>Displacement Test Number 1</u>				<u>Displacement Test Number 2</u>				<u>Displacement Test Number 3</u>			
W_i P.V.	ΔP psi	Injectivity $\Delta P_i/\Delta P$		W_i P.V.	ΔP psi	Injectivity $\Delta P_i/\Delta P$		W_i P.V.	ΔP psi	Injectivity $\Delta P_i/\Delta P$	
0	709	1.000		0	1071	1.000		0	989	1.000	
0.043	508	1.396		0.085	644	1.663		0.107	632	1.564	
0.248	131	5.412		0.108	588	1.821		0.205	474	2.086	
0.499	97	7.309		0.130	534	2.006		0.261	-	-	
1.059	73	9.712		0.184	416	2.575		0.550	167	5.922	
1.303	66	10.742		0.282	286	3.762		0.836	126	7.849	
1.577	43	16.488		0.520	226	4.739		1.112	-	-	
1.829	55	12.891		0.638	205	5.224		1.398	-	-	
2.133	-	-		0.727	182	5.884		1.669	-	-	
2.184	52	13.634		0.807	167	6.413		1.839	-	-	
				0.943	162	6.611		2.458	74	13.365	
				1.206	138	7.761		2.976	63	15.698	
				1.499	124	8.637		4.109	58	17.052	
				1.781	112	9.563		5.243	-	-	
				2.088	102	10.500					
				2.175	98	10.929					

TABLE C-7 (continued)

Displacement Test Number 4				Displacement Test Number 5				Displacement Test Number 6			
W _i P.V.	ΔP psi	Injectivity API/ΔP		W _i P.V.	ΔP psi	Injectivity API/ΔP		W _i P.V.	ΔP psi	Injectivity API/ΔP	
0	1216	1.000		0	1151	1.000		0	1143	1.000	
0.113	-			0.181	525	2.192		0.113	-	-	
0.279	581	2.093		0.254	374	3.078		0.281	357	3.202	
0.406	357	3.406		0.375	257	4.479		0.563	225	5.080	
0.707	354	3.435		0.529	201	5.726		0.838	177	6.457	
0.974	200	6.080		0.704	174	6.615		1.116	145	7.882	
1.095	182	6.681		0.740	172	6.692		1.358	109	10.486	
1.662	139	8.748		0.812	-	-		1.685	99	11.545	
2.800	-			1.009	139	8.281		1.917	93	12.290	
3.94	-			1.296	120	9.592		2.186	83	13.771	
5.07	-			1.648	101	11.396		2.252	-	-	
6.21	-			1.895	91	12.648		3.388	63	18.175	
7.34	53	22.943		2.451	65	17.707		4.522	60	19.050	
				3.009	53	21.717					

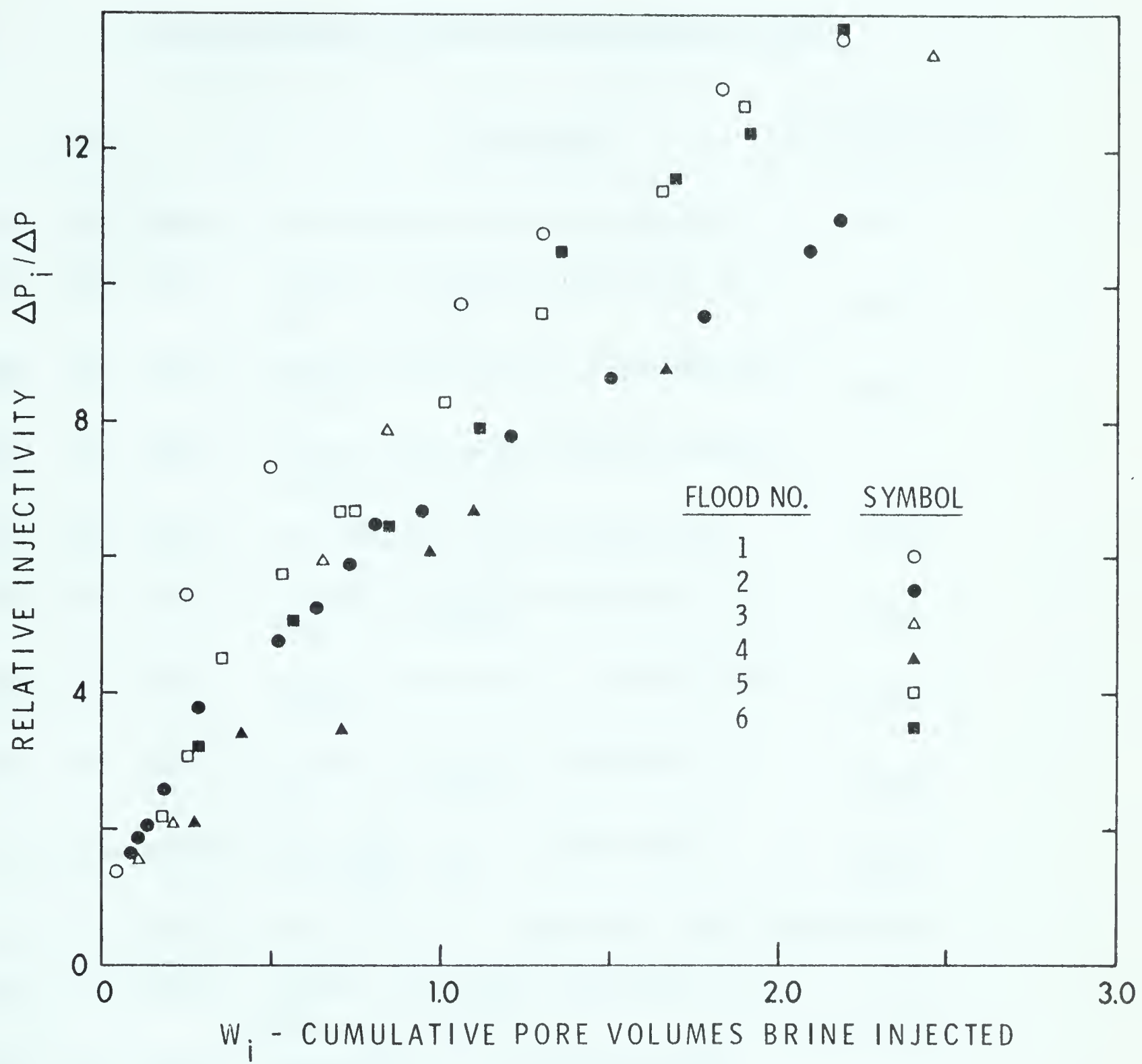


Figure C-5

INJECTIVITY AS A FUNCTION OF PORE VOLUMES INJECTED

TABLE C-8

Time Analysis of Core Displacement Tests

<u>Date</u>	<u>Operation</u>	<u>Fluid Injected (cc)</u>
Dec. 28, 1963	Artificial brine saturation	2000
Dec. 30, 1963	Lloyd "A" Crude injection to $S_{wc} = 0.283$	3169
May 15, 1964	Brine Flood No. 1 - artificial brine	1943
May 25, 1964	Clean core with varsol pentane propane and air	
June 16, 1964	Artificial brine saturation	890
June 17, 1964	Lloyd "A" Crude injection to $S_{wc} = 0.285$	970
June 22, 1964	Brine Flood No. 2 - artificial brine	1918
July 18, 1964	Lloyd "A" Crude injection to $S_{wc} = 0.309$	1958
July 28, 1964	Flood No. 3 - 0.005% NaOH (0.09011 gm)	1622
Aug. 4, 1964	Flood No. 3 - Continue with brine	3002
Aug. 6, 1964	Lloyd "A" Crude injection to $S_{wc} = 0.392$	965
Aug. 11, 1964	Flood No. 4 - 0.0001% NaOH (0.002742 gm)	2468
Aug. 24, 1964	Flood No. 4 - Continue with brine	4000
Aug. 27, 1964	Lloyd "A" Crude injection to $S_{wc} = 0.451$	989
Sept. 1, 1964	Flood No. 5 - Artificial brine	2654
Sept. 14, 1964	Lloyd "A" Crude injection to $S_{wc} = 0.501$	983
Sept. 20, 1964	Flood No. 6 - 0.005% NaOH (0.1104 gm)	1988
Sept. 30, 1964	Flood No. 6 - Continue with brine	2002

TABLE C-9

Relative Permeability Sample Calculation

Unsteady State Method of Welge(93)

Using Leverett's(61) fractional flow equation and neglecting capillary pressure and gravity terms

$$f_w = \frac{1}{1 + \frac{k_o \mu_w}{k_w \mu_o}}$$

rewriting

$$\frac{k_w}{k_o} = \frac{\mu_w}{\mu_o} \left(\frac{f_w}{1 - f_w} \right)$$

where

$$f_w + f_o = 1$$

$$WOR = \frac{\Delta W_p}{\Delta N_p}$$

$$f_o = \frac{\Delta N_p}{\Delta N_p + \Delta W_p}$$

$$= \frac{1}{1 + WOR}$$

then

$$\frac{k_w}{k_o} = \frac{\mu_w}{\mu_o} \frac{1 - f_o}{f_o}$$

TABLE C-9 (continued)

To calculate the downstream water saturation at the middle of the production interval

$$S_{wa} = \frac{W_p - \frac{1}{2} \Delta N_p}{PV} + S_{wc}$$

$$S_{wd} = S_{wa} - f_o \left[\frac{W_p + N_p - \frac{1}{2} (\Delta N_p + \Delta W_p)}{PV} \right]$$

The calculated relative permeability for Displacement Test No. 3 is shown in Table C-10.

TABLE C-10

Sample Relative Permeability Calculation
Displacement Test No. 3

$\mu_w/\mu_o = 0.8564$										$PV = 882\text{ cc}$		$S_{wc} = 0.309$	
Interval	ΔN_p	ΔW_p	N_p	W_p	WOR	f_o	k_w/k_o	S_{wa}	S_{wd}				
1	93	0	93	0	0	1.0000	0	0.3619	0.3092				
2	52	33	145	33	0.6346	0.6118	0.0005434	0.4441	0.3501				
3	33	21	178	54	0.6364	0.6111	0.0005450	0.4923	0.3496				
4	90	164	268	218	1.8222	0.3543	0.001561	0.5620	0.4178				
5	30	225	298	443	7.5000	0.1176	0.006426	0.6300	0.5482				
6	20	230	318	673	11.5000	0.08000	0.009849	0.6584	0.5799				
7	15	233	333	906	15.5333	0.06048	0.01330	0.6782	0.6018				
8	11	229	344	1135	20.8181	0.04583	0.01783	0.6930	0.6250				
9	7	143	351	1278	20.4285	0.04667	0.01749	0.7032	0.6236				
10	19	520	370	1798	27.3684	0.03525	0.02344	0.7179	0.6420				
11	14	248	384	2246	17.7142	0.05344	0.01517	0.7366	0.5852				
12	16	989	400	3235	61.8125	0.01592	0.05294	0.7536	0.6971				
13	5	995	405	4230	199.0000	0.005000	0.1704	0.7655	0.7421				

A P P E N D I X D

THE EFFECT OF SODIUM HYDROXIDE

ON NATURAL OIL FIELD BRINES

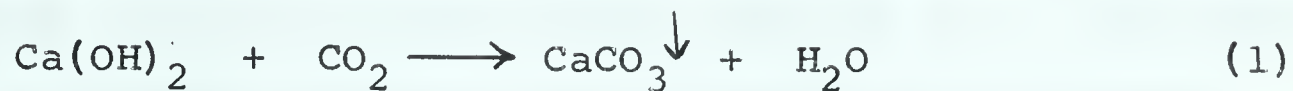
Investigation involving natural formation water from several areas indicates that a serious problem may be encountered when sodium hydroxide is added to these brines. Tests have been made on six water samples using 0.046 percent and 0.005 percent by weight sodium hydroxide (Table D-1). Results of these tests show that precipitate will form almost immediately upon the addition of sodium hydroxide to the brine.

Reviewing the solubilities of the various possible compounds which could be formed, it was noted that calcium carbonate or magnesium hydroxide would be precipitated from the waters tested when carbonate and bicarbonate ions are present in sufficiently high concentrations.

Immediately after the sodium hydroxide is added to a brine sample ionization takes place. Hydroxide ions are formed where previously no hydroxide ions existed (Table D-2). Calcium ions are already present in the listed brines in sufficient quantity to combine with any added hydroxide ion. With the presence of calcium hydroxide (lime) in ionized form, the common water softening reactions will occur.

Ryan(82) gives these reactions and notes that they will proceed in a systematic manner, limited by the solubilities of the various compounds involved. Calcium hydroxide combines with the carbon dioxide, calcium bicarbonate and magnesium bicarbonate in approximately that order.

The reactions are as follows:



Calcium carbonate and magnesium hydroxide will precipitate from the solutions until equilibrium is reached. Solubility for calcium carbonate is 14 milligrams per litre in pure water and magnesium hydroxide is 9 milligrams per litre. Reaction (3) above will only proceed if sufficient calcium hydroxide is available and if the concentration of magnesium carbonate becomes high. Reaction (3) can be considered as two successive reactions.



The solubility of magnesium carbonate is 106 milligrams per litre and as a result reaction (3) is the last one to go to completion.

A sample calculation (Table D-3) was made on the expected reaction of a Lloydminster brine sample to the addition of sodium hydroxide. The sample from well 2-24-50-2 W4 completed in the Sparky sand contained no hydroxide or carbonate ion and only 2 milligrams per litre of sulphate ion (Table D-2).

Assuming no carbon dioxide present, reaction (1) will not occur and reaction (2) will proceed before reaction (3). The complete reaction to calcium carbonate would require 144 milligrams per litre of sodium hydroxide to react with 219 milligrams per litre of calcium carbonate. Using the method of Stiff and Davis(85) and assuming the Langelier stability index is zero, P Alk is 3.7 and the solubility of carbonate ion is 12 milligrams per litre for the sample. As a result, 339 milligrams per litre of calcium carbonate will be precipitated.

This precipitation is a serious problem which must be solved before sodium hydroxide can be considered as a treatment for injection water. Two solutions are suggested for this problem. A standard lime treatment for water softening can be applied to the injection water or a "threshold treatment" of sodium hexametaphosphate could be considered.

The standard water softening treatment uses lime to precipitate the bicarbonate ions according to the reactions previously outlined. Lime is generally used because of low cost, although with the particular brines noted, sodium hydroxide would be equally effective because of the high calcium ion concentration. The precipitate formed from these reactions settles out slowly when allowed to stand. The addition of aluminum sulphate (alum) or sodium aluminate will accelerate the reactions and coagulate to assist in settling the precipitate.

A definite reduction in alkalinity can be noted in samples No. 2 and No. 4 against the alkalinity of samples No. 1 and No. 2, respectively (Table D-1). A larger reduction was expected based on the solubilities of the reaction components of the water softening process.

A second method, controlling the solubility of calcium carbonate, is worthy of consideration. This method called "threshold treatment" by Hatch(42) utilizes the surface active properties of sodium hexametaphosphate $(\text{NaPO}_3)_x$ to reduce or eliminate precipitation of calcium carbonate. Hexametaphosphate attaches at the solid-liquid interface of any forming crystal of calcium carbonate. A condition of supersaturation can then be maintained for the calcium carbonate. Hatch was able to maintain in solution 800 milligrams per litre of calcium carbonate using 2 milligrams per litre of sodium hexametaphosphate.

Hatch has also demonstrated that deposition from supersaturated solutions of calcium carbonate is limited by addition of hexametaphosphate to the solution. It was found, on passage of a supersaturated solution of calcium carbonate containing 2 milligrams per litre of sodium hexametaphosphate through calcium carbonate encrusted sand, that calcium carbonate initially deposited on the sand but, in a very short time, no further deposition occurred.

The sodium hexamethophosphate treatment is also effective for magnesium carbonate. Unfortunately, this treatment is not effective for magnesium hydroxide. In the case

where chemical reaction (3) or (5) go to completion, a precipitate would still be expected.

Johansen(49) also found that the polyphosphates, in particular sodium tripolyphosphate, reversed the wettability of a sand from oil wet to water wet. This chemical has been field tested by Johansen(50) and improved water injectivity was noted. The research concluded to data indicates further possibilities for applying this group of chemical additives.

This information is presented only as a preliminary approach to the problem. Use of fresh water containing very small amounts of bicarbonate and carbonate ions could simplify the treatment but consideration must be given to the effect of mixing in the reservoir.

TABLE D-1

Chemical Analysis of Water Samples - Parts Per Million

	1	2	3	4	5	6	7	8	9
Total Solids	92,118	91,000	250,640	271,800	94,400	107,200	103,220	91,128	84,839
Ignition Loss	9,452	14,200	51,150	85,400	21,400	10,580	17,380	10,144	
Hardness	12,150	1,000	24,250	1,000	1,000	1,000	1,000	1,000	
Sulphates								178	
Chlorides	50,002	46,545	120,375	112,970	53,000	67,800	51,985	48,800	51,467
Alkalinity	290	105	310	70	210	35	115	265	
Iron	14	-	4	-	10	5	-	1.0	
pH	6.9	9.6	6.2	7.5	6.6	3.1	7.1	6.8	6.55
pH after adding 0.005% NaOH	8.0		7.1		7.7	4.5	8.0	8.0	10.45
Alkalinity - $\text{Ca}(\text{HCO}_3)_2$ - $\text{Mg}(\text{HCO}_3)_2$									
Samples:	1.	Fargo #21	injection well						
	2.	Fargo #21	injection well	with 0.046% by weight	sodium hydroxide				
	3.	Fargo #60							
	4.	Fargo #60	with 0.046% by weight	sodium hydroxide					
	5.	Husky Aberfeldy B-4-33-49-26-W3	Sparky Sand						
	6.	Lloydminster area sample							
	7.	Devon Palmer Battery #1	- Chauvin						
	8.	Provo Hughendon 6-27	- Basal Quartz						
	9.	Artificial Brine							

TABLE D-2

Chemical Analyses of Typical Water Samples (6)

	<u>Lloydminster Sparky</u>	<u>Lloydminster-Sparky</u>	<u>Chauvin Sparky</u>
	<u>Solids (Mg/Litre)</u>		
Location	Lloydminster Area	2-24-50-2-W4	16-11-43-1-W4
Chloride	51,467	56,441	39,126
Bromide	195	256	156
Iodide	12	11	9
Carbonate	0	0	0
Bicarbonate	118	219	365
Hydroxide	0	0	-
Sulphate	2	2	7
Calcium	3,540	4,990	2,317
Magnesium	1,681	2,359	724
Sodium (Calculated*)	26,243	26,578	21,536
Total solids (calc.)	83,258	90,856	64,240
Total solids (after ignition)	81,830	98,460	62,790
Density (60°F)	1.0583	1.0632	1.045
pH	6.2	6.4	6.8

* Alkali metals calculated as sodium

TABLE D-3

Calculation of Calcium Carbonate Precipitate
Formed by a Typical Brine

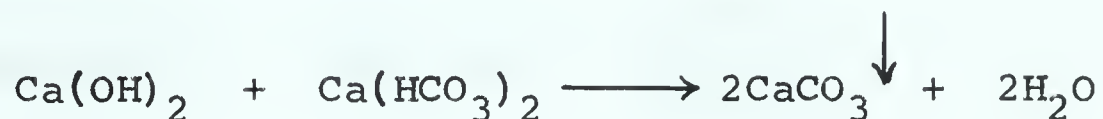
Example Brine - Lloydminster Sparky 2-24-50-2-W4

Analysis: Bicarbonate 219 PPM

Carbonate 0 PPM

Calcium 4990 PPM

On addition of sufficient NaOH the following reaction will occur after ionization. Both Ca^+ and OH^- ions will be present along with HCO_3^-



Assuming that the reaction is 100% complete, which is the worst case, one molecule of CaCO_3 will be formed for each ion of HCO_3^- originally present

$$\text{CaCO}_3 \text{ PPM} = \text{HCO}_3^- \text{ PPM} \times \frac{100.019}{61.019}$$

$$= 219 (1.6403)$$

$$= 359 \text{ PPM}$$

$$\text{CO}_3^{--} \text{ PPM} = 359 \text{ PPM} \times \frac{60.011}{100.091}$$

$$= 215 \text{ PPM}$$

TABLE D-3 (continued)

Solubility of CaCO_3 is 14 PPM in pure water (reference 41)
For water in equilibrium the Langelier stability index is 0

$$\therefore 0 = \text{pH} - \text{pCa} - \text{pAlk} - K$$

By trial and error the amount of CaCO_3 which will stay in solution can be obtained using the method of Stiff and Davis(86).

For each ion of HCO_3^- one NaOH must be added to the solution for reaction

$$\begin{aligned} \text{NaOH PPM} &= \text{HCO}_3^- \text{ PPM} \times \frac{39.999}{61.019} \\ &= 219 (0.6556) \\ &= 144 \text{ PPM} \end{aligned}$$

$\therefore$

$$\begin{aligned} \text{Na}^+ \text{ added} &= 144 \left(\frac{22.991}{39.999} \right) \\ &= 83 \text{ PPM} \end{aligned}$$

The ionic strength of Lewis and Randall(64) is

$$u = 0.5 (C_1 V_1^2 + C_2 V_2^2 + C_3 V_3^2 + \dots)$$

where

C_1 = gram ions per 1000 grams of solvent

V_1 = valence of the ion

TABLE D-3 (continued)

For this sample

$$\begin{aligned}
 u &= 0.5 \left(\frac{56.441}{35.457} + \frac{0.256}{79.919} + \frac{0.011}{126.91} + \frac{0.144(4)}{60.11} \right. \\
 &\quad \left. + \frac{0.002(4)}{96.066} + \frac{4.990(4)}{40.08} + \frac{2.359(4)}{24.32} + \frac{26.661}{22.991} \right) \\
 &= 1.825
 \end{aligned}$$

$$\therefore K = 1.805 \quad (\text{Figure 1 - Stiff and Davis})$$

$$\begin{aligned}
 \therefore pAlk &= pH - pCa - K \\
 pAlk &= 6.4 - 0.90 - 1.805 \\
 &= 3.7
 \end{aligned}$$

$$CO_3^{--} \text{ equilibrium} = 12 \text{ PPM}$$

$$\begin{aligned}
 CO_3^{--} \text{ precipitated as CaCO} &= 215 - 12 \\
 &= 203 \text{ PPM}
 \end{aligned}$$

$$\begin{aligned}
 CaCO_3 \text{ precipitated} &= 203 \text{ PPM} \times \frac{100.091}{60.011} \\
 &= 339 \text{ PPM}
 \end{aligned}$$

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